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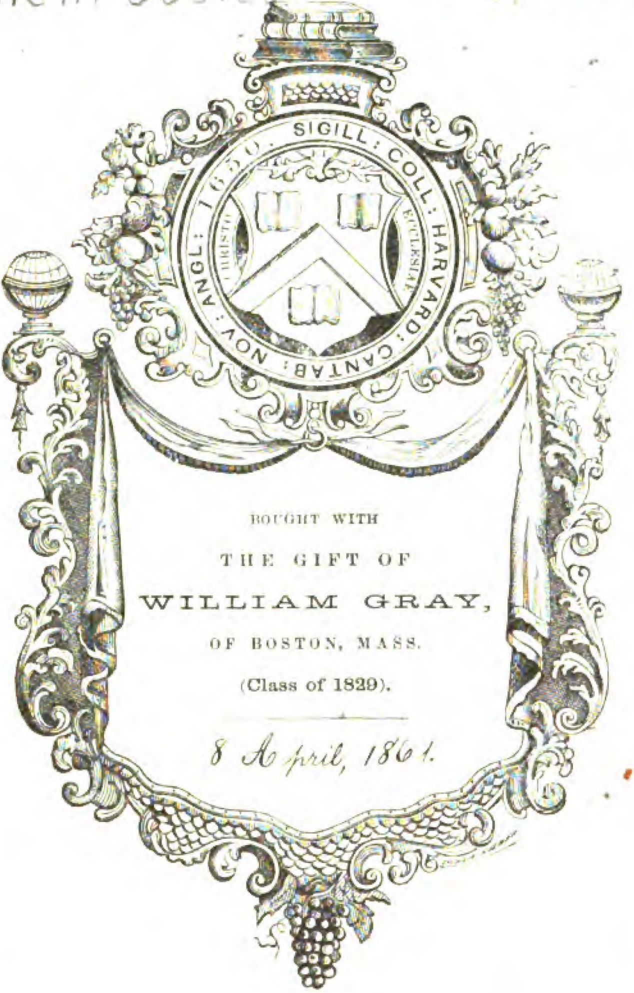

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IN

QUANTITATIVE CHEMICAL ANALYSIS.

BY

DR. C. REMIGIUS FRESENIUS,

PROFESSOR OF CHEMISTRY AND NATURAL PHILOSOPHY, WIESBADEN.

Third Edition.

EDITED BY

J. LLOYD BULLOCK, F.C.S.

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PREFACE.

The great reputation so long enjoyed by the two works of Dr. Fresenius on Qualitative and Quantitative Analysis, has in no degree abated the Author's exertions to improve them, and to maintain their pre-eminent position.

In the preface to the former edition of the Quantitative Analysis, I observed:—

"The Author has spared no pains or labor, not merely to keep it up to the improved state of the science, but to make it the medium of introducing methods of research in advance of all other works. Whatever has been proposed, either in this country or on the Continent, to facilitate the path of analysis, has been tested, and, when found sound and practical, has been introduced in its proper place. Every doubtful point has been rigidly subjected to repeated experiments, errors corrected and faults amended, and many new processes added from the Author's ample experience in his own laboratory."

Among the additions there introduced, the volumetrical methods of determining the constituents of commercial articles were pointed out as particularly important for economizing time, and assisting in every way the practical chemist.

The present edition, which corresponds with the fourth German, is rendered far more valuable than its predecessors.

The entire work has been re-cast, considerably simplified, and almost re-written. New matter has been introduced, to the extent of one-fourth of the whole volume. Many of the processes—the best then known, but rendered obsolete by the progress of the science—have been replaced by others more certain, simple, and efficient; and this is particularly the case with the volumetrical processes.

Among other changes, I may specify the analytical processes for clays, soils, cast iron, atmospheric air, and lead ores.

This work on QUANTITATIVE ANALYSIS, although in itself complete, may be regarded as a sequel to the author's QUALITATIVE ANALYSIS—a work which has been found of the highest value—nay, almost indispensable—to the student of Chemistry, whatever other books on the subject he may possess.

As a guide to Analytical Chemistry, the merits of the present volume are of the highest order. The arrangement is simple, methodical, and consecutive; the theoretical explanations are appropriate, clear, and intelligible; the language plain, and the directness and honesty of purpose, together with the just appreciation of the labors of others, displayed throughout, must commend it to every one engaged in studying, teaching, or practising Chemistry; and I have great pleasure in being the medium of presenting it to the English public.

J. LLOYD BULLOCK.

3, *Hanover-street, Hanover-square, W.*

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INTRODUCTION.

In my treatise entitled, "Elementary Instruction in Qualitative Chemical Analysis," I have stated that **analytical chemistry** comprehends two branches, viz., "*qualitative analysis*," and "*quantitative analysis*," and that the object of the former is to ascertain the individual *kind and nature*, that of the latter to determine the absolute and relative *quantity or proportion* of the several component parts of any given compound.

By **qualitative analysis** we convert the *unknown* constituents of a given compound into certain forms or combinations with the properties of which we are acquainted; and we are thus enabled to draw correct inferences respecting the nature of *every individual constituent* of the compound in question. Quantitative analysis attains its object, according to circumstances, often by very different ways; the two methods most widely differing from each other, are "*analysis by weight*," or *gravimetrical analysis*, and "*analysis by measure*," or "*volumetrical analysis*."

Quantitative analysis by weight, or gravimetrical analysis, has for its object to convert the *known* constituents of a given compound into such forms or combinations as will admit of the most exact determination of their weight, and of which, moreover, the relative and combining proportions are accurately known. These new forms or combinations may be either *educts* from the analysed compound or mixture, or they may be *products*. In the former case we have simply to weigh the eliminated substance, since its ascertained weight, of course, supplies at once the direct expression of the quantity, or proportion in which it existed in the compound under examination; whilst in the latter case, that is, when we have to deal with *products*, the quantity, or proportion in which the eliminated constituent was originally present in the analysed compound, has to be deduced by calculation from the proportion in which it exists in its new combination.

The following example will serve to illustrate these points:—Suppose we wish to determine the proportional amount of mercury contained in the chloride of that metal; now, we may do this, either by precipitating the metallic mercury from the solution of the chloride, by means of protochloride of tin; or we may attain our object by precipitating the solution of chloride of mercury by sulphuretted hydrogen, and weighing the precipitated sulphide of mercury. 100 parts of chloride of mercury consist of 73·83 of mercury and 26·17 of chlorine; consequently, the precipitation of a solution of chloride of mercury by protochloride of tin will yield 73·83 per cent. of metallic mercury, which may be verified by simply weighing the precipitated metal. The precipitation of the same amount of chloride of mercury, by means of sulphuretted hydrogen, yields 85·638 of sulphide of mercury.

Now, in the former case the number 73·83 expresses *directly* the proportion of mercury contained in the analysed chloride; in the latter case we have to deduce this proportion by calculation, which may be accomplished by means of the following simple equation:—100 parts of sulphide of mercury contain 86·213 parts of mercury; how much mercury do 85·638 parts contain?

$$100 : 86{\cdot}213 :: 85{\cdot}638 : x = 73{\cdot}83.$$

It will be readily understood from the preceding illustration, that all those forms and combinations into which the known constituents of a given compound are to be converted for the purpose of quantitative estimation must, of necessity, in the first place, admit of most accurate weighing, and that, in the second place, their composition must be correctly known. These two conditions are absolutely indispensable; for it is quite obvious, on the one hand, that accurate quantitative analysis must be altogether impossible if the substance the quantity of which it is intended to ascertain does not admit of correct weighing; and, on the other hand, it is equally evident, that if we do not know the exact composition of a new product, we lack the most indispensable element for our subsequent deductions.

ANALYSIS BY MEASURE, OR VOLUMETRICAL ANALYSIS, is based upon a very different principle from that of analysis by weight; viz., it effects the quantitative determination of a body, by converting it from a certain definite state to another equally definite state, by means of a fluid of accurately known composition and action, and under circumstances permitting the analyst to mark with rigorous precision the exact point when the conversion is accomplished and terminated. The following example will serve to illustrate the principle of this method:—Permanganate of potassa added to a solution of sulphate of protoxide of iron, acidified with sulphuric acid, immediately converts the protoxide of iron to sesquioxide; the permanganic acid, which is characterized by its intense color, yielding up oxygen and changing to protoxide of manganese, which combines with the sulphuric acid present to colorless sulphate of protoxide of manganese. If, therefore, to an acidified fluid containing protoxide of iron, we add, drop by drop, a solution of permanganate of potassa, the red color imparted to the fluid by every fresh drop added, continues for some time to disappear again upon stirring; but at last a point is reached when the coloration imparted to the fluid by the last drop added remains: this point marks the termination of the conversion of the protoxide of iron to sesquioxide.

Now, by accurately determining the strength, or power of action of the solution of permanganate of potassa—which is done simply by making it act upon a known quantity of protoxide of iron in solution, and correctly noting how much of it is required to effect the conversion of that protoxide to the state of sesquioxide—we get a standard which will enable us to determine the exact amount of protoxide of iron present in any given solution. Thus, we will assume, for instance, that we have found it takes exactly 100 parts of our solution of permanganate of potassa to peroxidize 2 parts of protoxide of iron; if now, in testing, with this standard solution of permanganate of potassa any given solution containing protoxide of iron in unknown proportion, we find that

100 parts of our standard fluid are required to peroxidize the iron, we know at once that the examined fluid contained exactly 2 parts of protoxide of iron; if 50 parts are required, we know that 1 part of protoxide of iron was present, &c. &c. Accordingly, by simply measuring the quantity used of our standard solution of permanganate of potassa, we arrive at once at an accurate knowledge of the corresponding amount of protoxide of iron.

As the process of measuring is mostly resorted to, in preference to that of weighing, for determining the quantity used of the standard fluid, we give to this analytical method the name of analysis by measure, or volumetrical analysis. It generally leads to the attainment of the object in view with much greater expedition than is the case with analysis by weight.

To this brief intimation of the general purport and object of quantitative analysis and the general mode of proceeding in analytical researches, I have to add that certain qualifications are essential to those who would devote themselves successfully to the pursuit of this important branch of the science of chemistry. These qualifications, are, 1, theoretical knowledge; 2, skill in manipulation; and 3, strict conscientiousness.

The preliminary *theoretical knowledge* required consists in an acquaintance with the qualitative branch of analytical chemistry; together with some practice in simple arithmetic. A previous knowledge of qualitative analysis enables us to understand all the various methods proposed for isolating substances in order to determine their weight; whilst practice in simple arithmetical calculations enables us to deduce from our analytical results the composition of the analysed substance in equivalents, to test the correctness of the method we have pursued, and to control the results arrived at. To this *knowledge* must be joined the *ability of performing the necessary practical operations.* This is an axiom generally applicable in all practical sciences, but more particularly in quantitative chemical analysis. The most extensive and solid theoretical acquirements will not enable us, for instance, to determine the amount of common salt present in a solution of that substance, if we are without the requisite dexterity to transfer a fluid from one vessel to another without the smallest loss. The various operations of quantitative analysis demand great aptitude and manual skill, which can be acquired only by practice. But even the possession of the greatest practical skill in manipulation, joined to a thorough theoretical knowledge, will still prove insufficient to insure a successful pursuit of quantitative researches, *unless combined also with a sincere love of truth and a firm determination to accept none but thoroughly verified and confirmed results.*

No one who has ever been engaged in quantitative analysis can deny that cases will sometimes happen in which doubts may be entertained as to whether the results of the operation are correct, or even where the operator is *positively convinced* that the result of his process *cannot* be *quite* correct. Thus, for instance, a small portion of the substance under investigation may be spilled, or some of it lost by decrepitation; or the analyst may have reason to doubt the accuracy of his weighing; or it may happen that two analyses of the same substance do not exactly agree. In all such cases it is indispensable that the operator should be conscientious enough to repeat the whole process over again. He who is not animated with this sincere devotion to science and is afraid of encountering labor and difficulties in the pursuit of truth—he who would be satisfied with mere assumptions or suppositions and guess-work, where the attainment of positive certainty is the object, must be pronounced just as deficient in the necessary qualifications for quantitative analytical researches, as he who is wanting in theoretical knowledge or in practical skill. He, therefore, who cannot firmly and fully rely upon the accuracy of his operations and labors—he who cannot *swear* to the correctness of his results, may indeed occupy himself with quantitative analysis for his own private amusement, but he ought never to *publish* as correct and *positive* the results of his operations and researches, since such a proceeding might be eminently injurious to others, by misleading them and might, in the end, even prove greatly detrimental to the interests of true science; nor would it be prudent for him to apply such results to any practical purpose of his own, since this would be sure to turn out very little advantageous to himself.

The domain of quantitative analysis may be said to extend over all matter, that is, in other words, anything corporeal may become the object of quantitative investigation. The present work, however, is intended to embrace only the substances used in pharmacy, arts, trades, agriculture, and manufactures.

Quantitative analysis may be subdivided into two branches, viz., analysis of *mixtures*, and analysis of *chemical compounds*. This division may appear at first sight of very small moment, yet it is necessary that we should establish and maintain it, if we would form a clear conception of the value and utility of quantitative research. The quantitative analysis of mixtures has not the same aim as that of chemical compounds; and the method applied to secure the correctness of the results in the former case is different from that adopted in the latter. The quantitative analysis of chemical compounds rather subserves the theoretical purposes of science, whilst that of mixtures belongs to the practical purposes of life. If, for instance, I analyse the salt of an acid, the result of the analysis will give me the constitution of that acid, its combining proportion, saturating capacity, &c. &c.; or, in other words, the results obtained will enable me to answer a series of questions of which the solution is important for the theory of chemical science: but if, on the other hand, I analyse gunpowder, alloys of metals, medicinal mixtures, ashes of plants, &c. &c., I have a very different object in view; I do not want in such cases to apply the results which I may obtain to the solution of any theoretical question in chemistry, but I want to render a practical service either to the arts, trades, or manufactures, or to some other science. If in the analysis of a chemical compound, I wish to control the results obtained, I may do this in most cases by means of calculations based on stœchiometric data, but in the case of a mixture a second analysis is necessary to *confirm* the correctness of the results afforded by the *first*.

The preceding remarks clearly show the immense importance of quantitative analysis. It may, indeed, be averred that chemistry owes to this branch its elevation to the rank of a science, since quantitative researches have led us to discover and determine the laws which govern the combinations and transpositions of the elements. Stœchiometry is entirely based upon the results of quantitative investigations; all rational views respecting the constitution of compounds rest upon them as the only safe and solid basis.

Quantitative analysis, therefore, forms the strongest and most powerful lever for chemistry as a science, and not less so for chemistry in its applications to the practical purposes of life, to trades, arts, manufactures, and likewise in its application to other sciences. It teaches the mineralogist the true nature of minerals, and suggests to him principles and rules for their recognition and classification. It is an indispensable auxiliary to the physiologist; and no one can deny that agriculture has derived of late, and will continue to derive, incalculable benefit from it. We need not expatiate here upon the advantages which medicine, pharmacy, and every branch of industry derive, either directly or indirectly, from the practical application of its results. On the other hand, the benefit thus bestowed by quantitative analysis upon the various sciences, arts, &c., has been in some measure reciprocated by some of them. Thus whilst stœchiometry owes its establishment to quantitative analysis, the stœchiometrical laws afford us the means of controlling the results of our analyses so accurately as to insure their correctness, and to justify the reliance which we now generally place on them. Again, whilst quantitative analysis has advanced, and continues to advance, the progress of arts and industry, our manufactures in return supply us with the most perfect platinum- glass- and porcelain-vessels, and articles of india-rubber, without which it would be next to impossible to conduct our analytical operations with the minuteness and accuracy to which we have now attained.

Although the aid which quantitative analysis thus derives from stœchiometry, and the arts and manufactures, greatly facilitate its practice, it must be admitted that the pursuit of this branch of chemistry to any satisfactory purpose, requires, notwithstanding, considerable expenditure of time. I would therefore advise every one desirous of becoming an analytical chemist, to arm himself with a considerable share of patience, reminding him that it is not at one bound, but gradually, and step by step, that the student may hope to attain to that skill and precision in his operations that may justify reliance upon the correctness of his results. However mechanical, protracted, and tedious the operations of quantitative analysis may appear to be, the attainment of accuracy will amply compensate for the time and labor bestowed upon them; whilst, on the other hand, nothing can be more disagreeable than to find, after a long and laborious process, that our results are incorrect or uncertain. Let him, therefore, who would render the study of quantitative analysis agreeable to himself, from the very outset endeavor, by strict, nay, scrupulous adherence to the rules and conditions of this science, to attain to correct results, at any sacrifice of time. There cannot be a better and more immediate reward of labor than that which springs from the attainment of accurate results and perfectly corresponding analyses. The satisfaction enjoyed at the success of our efforts is surely in itself a sufficient motive for the necessary expenditure of time and labor, even without looking to the practical benefits which we may derive from our operations.

The following are the substances treated of in this work :—

I. Metalloids, or Non-Metallic Elements.

Oxygen, Hydrogen, Sulphur, [*Selenium,*] *Phosphorus, Chlorine, Iodine, Bromine, Fluorine, Nitrogen, Boron, Silicon, Carbon.*

II. METALS.

Potassium, Sodium, [Lithium,] Barium, Strontium, Calcium, Magnesium, Aluminium, Chromium, [Titanium,] Zinc, Manganese, Nickel, Cobalt, Iron, [Uranium,] Silver, Mercury, Lead, Copper, Bismuth, Cadmium, [Palladium,] Gold, Platinum, Tin, Antimony, Arsenic, [Molybdenum].

The elements enclosed within brackets are considered in supplementary paragraphs, and more briefly than the other elements.

I have divided my subject into three parts. In the first, I treat of quantitative analysis generally; describing, 1st, the methods of performing analytical operations and processes; and, 2nd, the calculation of the results obtained. In the second, I give a detailed description of several special analytical processes. And in the third, a number of carefully selected examples, which may serve as exercises for the groundwork of the study of quantitative analysis.

The following table will afford the reader a clear and definite notion of the contents of the whole work:—

I. GENERAL PART.

A—DESCRIPTION OF THE ANALYTICAL METHODS AND PROCESSES.

1. Operations.
2. Reagents.
3. Forms and combinations in which substances are separated from others, or in which their weight is determined.
4. Determination of the weight of substances in simple compounds.
5. Separation of substances.
6. Organic elementary analysis.

B—CALCULATION OF THE RESULTS.

II. SPECIAL PART.

1. Analysis of natural springs, and more especially of mineral waters.
2. Analysis of such minerals and technical products as are most frequently brought under the notice of the chemist; with comprehensive methods for ascertaining their commercial value.
3. Analysis of the ashes of plants.
4. Analysis of soils.
5. Analysis of manures.
6. Analysis of atmospheric air.

III. EXERCISES FOR PRACTICE.

APPENDIX.

1. Analytical notes and experiments.
2. Tables for the calculation of analytical results.

DIVISION I.

GENERAL PART.

SECTION I.

ON THE METHODS OF PERFORMING ANALYTICAL PROCESSES.

CHAPTER I.

OPERATIONS.

§ 1.

Most of the operations performed in quantitative research are the same as in qualitative analysis, and have been accordingly described in my work on that branch of analytical science. With respect to such operations I shall, therefore, confine myself here to pointing out any modifications they may require to adapt them for application in the quantitative branch; but I shall, of course, give a full description of such as are resorted to exclusively in quantitative investigations. Operations forming merely part of certain specific processes will be found described in the proper place, under the head of such processes.

I. Determination of the Quantity.

§ 2.

The quantity of solids, and generally also that of fluids, is determined by *weight*; the quantity of gases, and often also of fluids, by *measure*; upon the care and accuracy with which these operations are performed, depends the value of all our results; I shall therefore dwell minutely upon them.

§ 3.

1. Weighing.

To enable us to determine with precision the correct weight of a substance, it is indispensable that we should possess, 1st, a good BALANCE, and 2nd, perfectly accurate WEIGHTS.

a. The Balance.

There are several points respecting the construction and properties of a good balance, which it is absolutely necessary for every chemist to understand. The usefulness of this indispensable instrument of quantitative chemistry depends upon two points; 1st, its *accuracy*, and 2nd, its *sensibility* or *delicacy*.

§ 4.

The ACCURACY of a balance depends upon the following conditions:—

α. The fulcrum must be placed above the centre of gravity of the beam.

This is a condition essential to every balance. If the fulcrum were placed *in* the centre of gravity of the beam, the balance would not oscillate, but remain in any position in which it is placed, assuming the scales to be equally loaded. If the fulcrum be placed below the centre of gravity of the beam, the balance will be overset by the slightest impulse.

When the fulcrum is above the centre of gravity of the beam the balance represents a pendulum, the length of which is equal to that of the line uniting the fulcrum with the centre of gravity, and this line forms right angles with the beam in whatever position the latter may be placed. Now if we impart an impetus to a ball suspended by a thread, the ball, after having terminated its vibrations, will invariably fall back into its original perpendicular position under the point of suspension. It is the same with a properly adjusted balance—impart an impetus to it, and it will oscillate for some time, but it will *invariably* return to its original position; in other words, its centre of gravity will finally fall back into its perpendicular position under the fulcrum, and the beam must consequently reassume the horizontal position.

But to judge correctly of the force with which this is accomplished, and the velocity of the oscillations of a balance, it must be borne in mind that a balance is not a simple pendulum, but a compound one, *i.e.*, a pendulum in which not one, but many material points move round the turning point, or pole. The inert mass to be moved is accordingly equal to the sum of these points, and the moving force is equal to the excess of the material points below over those above the fulcrum.

β. The suspension points of the scales must be on an exact level with the fulcrum. If the fulcrum be placed below the line adjoining the points of suspension, increased loading of the scales will continually tend to raise the centre of gravity of the whole system, so as to bring it nearer and nearer the fulcrum; the weight which presses upon the scales combining in the relatively high-placed points of suspension; at last, when the scales have been loaded to a certain degree, the centre of gravity will shift altogether to the fulcrum, and the balance will consequently cease to vibrate—any further addition of weight will finally cause the beam to overset, by placing the centre of gravity above the fulcrum. If, on the other hand, the fulcrum be placed above the line joining the points of suspension, the centre of gravity will become more and more depressed in proportion as the loading of the scales is increased; the line of the pendulum will consequently be lengthened, and a greater force will be required to produce an equal turn; in other words, the balance will grow the less sensible the greater the load. But when the three edges are placed on a level with each other, increased loading of the scales will, indeed, continually tend to raise the centre of gravity towards the fulcrum, but the former can in this case never *entirely* reach the latter, and consequently the balance will never altogether cease to vibrate upon the further addition of weight, nor will its sensibility be lessened; on the contrary, a greater degree of sensibility is imparted to it. This increase of sensibility is, however, compensated for by other circumstances.

γ. The beam must be sufficiently strong and inflexible to bear without bending the greatest weight that the construction of the balance admits of;

since the bending of the beam would of course depress the points of suspension so as to place them below the line of the fulcrum, and this would, as we have just seen, tend to diminish the sensibility of the balance in proportion to the increase of the load. It is, therefore, necessary to avoid this fault by a proper construction of the beam. The form best adapted for beams is that of a rhomb, or of an equicrural obtuse-angled triangle.

δ. *The arms of the balance must be of equal length*, i.e., *the points of suspension must be equidistant from the fulcrum, or point of support;* for if the arms be unequal, the weights in equipoise will be unequal in the same proportion; *i.e.* the weights in one scale, acting upon the longer arm of the lever, will preponderate over the exact equivalent in the other scale, and this in direct proportion to the greater or lesser excess of length of one arm over the other.

§ 5.

The SENSIBILITY, or DELICACY of a balance depends principally upon the following conditions:—

α. *The friction of the edges upon their supports must be as slight as possible.* The greater or lesser friction of the edges upon their supports depends upon both the form and material of those parts of the balance. The edges *must* be made of good steel, the supporters *may* be made of the same material; it is better, however, that the centre edge should rest upon a perfectly horizontal agate plane. To form a clear conception of how necessary it is that even the lateral edges should have as little friction as possible, we need simply reflect upon what would happen were we to fix the scales in immovable points by means of inflexible rods. Such a contrivance would at once altogether annihilate the sensibility of a balance, for if a weight were placed upon one scale, this certainly would sink; but at the same time, being compelled to form constantly a right angle with the beam, it would incline inwards, whilst the other scale would turn outwards, and thus the weight would be made to act upon the shorter arm of the lever. The more considerable the friction becomes at the end edges of a balance, the more the latter approaches the state just now described, and consequently the more is its sensibility impaired.

β. *The centre of gravity must be as near as possible to the fulcrum.* The nearer the centre of gravity approaches the fulcrum, the shorter becomes the pendulum. If we take two balls, the one suspended from a short, and the other from a long thread, and impart the same impetus to both, the former will naturally, in the extent of its vibrations, swing at a far greater angle from its perpendicular position than the latter. The same must of course happen with a balance; the same weight will cause the scale upon which it is placed to turn the more rapidly and completely, the shorter the distance between the centre of gravity and the fulcrum. We have seen above, that in a balance where the three edges are on a level with each other, increased loading of the scales will continually tend to raise the centre of gravity towards the fulcrum. A good balance will therefore become more delicate in proportion to the increase of weights placed upon its scales, but, on the other hand, its sensibility will be diminished in about the same proportion by the increment of the mass to be moved, and by the increased friction attendant upon the increase of load; in other words, the delicacy of a good balance will remain the same whatever may be the load placed upon it, ranging from the minimum to the maximum that its construction will enable it to bear.

γ. *The beam must be as light as possible.* The remarks which we have just now made will likewise show how far the weight of the beam may influence the sensibility of a balance. We have seen that it is necessary that a balance should increase in delicacy in proportion to the increase of load, since the increased friction tends to diminish its delicacy in the same proportion; and further, we have seen that this increase in sensibility is owing to the increased weight continually tending to raise the centre of gravity towards the fulcrum. Now it is evident, that the more considerable the weight of the beam is, the less will an equal load placed upon both scales alter the centre of gravity of the whole system, the more slowly will the centre of gravity approach the fulcrum, the less will the increased friction be neutralized, and consequently the less sensibility will the balance possess. Another point to be taken into account here is, that the respective moving forces being equal, a lesser mass or weight is more readily moved than a larger one (compare § 4, *a*).

§ 6.

We will now proceed, first, to give the student a few general rules to guide him in the purchase of a balance intended for the purposes of quantitative analysis; and, secondly, to point out the best method of testing the accuracy and sensibility of a balance.

1. A balance able to bear 70 or 80 grammes in each scale, suffices for most purposes.

2. The balance must be enclosed in a glass-case to protect it from dust. This case ought to be sufficiently large, and, more especially, its sides should not approach too near the scales. It must be constructed in a manner to admit of its being closed with facility when the weights have been placed on the scales, and thus to allow the operation of weighing being effected without any disturbing influence from currents of air. Therefore, either the front part of the case should consist of three parts, viz., a fixed centre piece and two lateral parts, opening like doors; or, if the front part happens to be made of one piece, and arranged as a sliding-door, the two sides of the case must be provided each with a door.

3. The balance must be provided with a proper contrivance to render it immovable whilst the weights are being placed upon the scales. This is most commonly effected by an arrangement which enables the operator to lift up the beam and thus to remove the fulcrum from its support, whilst the scales remain suspended; other contrivances fix the scales, and leave the fulcrum resting on its support.*

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* One of my balances (made by the late M. Hoss, of Giessen) is so arranged, that whilst the beam is lifted up by *one* stop, the scales may be supported from beneath, and thus fixed, by *another* independent contrivance, which is worked and regulated from the side. The movable supports which constitutes one of the principal parts of this contrivance are provided at the top with crossed silk bands, and move with such perfect steadiness, that the scales do not shake in the least upon the removal of the supports from beneath them (provided, of course, the operation be effected with some degree of delicacy and caution). This arrangement, besides facilitating the loading of the scales, affords this advantage—that it enables the operator to put an immediate stop to all trembling or shaking of the scales, and also the convenience that, in cases where one and the same body,

But whatever contrivance may be had recourse to, at all events it is highly advisable to have the case of the balance so arranged that the processes of lifting up the beam, fixing the scales, &c., can be conducted while the case remains closed, and consequently from without.

4. It is necessary that the balance should be provided with an index to mark its oscillations; this index is more appropriately placed at the bottom than at the side of the balance.

5. The balance must be provided with a pendulum, or with a spirit level, to enable the operator to place the three edges on an exactly horizontal level; it is best also for this purpose that the case should rest upon three screws.

6. It is very desirable that the beam should be graduated into decimals, so as to enable the operator to weigh the milligramme and its fractions, by suspending a centigramme rider, or hook, on or between the indicated points of a graduated line, instead of placing the weight on the scale. Most modern balances are so constructed that the position of the riders on the beam may be shifted at pleasure, and without opening the glass case, by means of a movable arm placed in the side of the case.

7. The balance must be provided with a screw to regulate the centre of gravity, and likewise with two screws to regulate the equality of the arms, and finally with screws to restore instantly the equilibrium of the scales, should this have been disturbed.

§ 7.

The following experiments serve to test the accuracy and sensibility of a balance.

1. The balance is, in the first place, accurately adjusted, if necessary, either by the regulating screws, or by means of tinfoil, and a milligramme weight is then placed in one of the scales. A good and practically useful balance must turn distinctly with this weight; a delicate chemical balance should indicate the $\frac{1}{10}$ of a milligramme with perfect distinctness.

2. Both scales are loaded with the maximum weight the construction of the balance will admit of—the balance is then *accurately* adjusted, and a milligramme added to the weight in the one scale. This ought to cause the balance to turn to the same extent as in 1. In most balances, however, it shows somewhat less on the index.

3. The balance is accurately adjusted, (should it be necessary to establish a perfect equilibrium between the scales by loading the one with a minute portion of tinfoil, this tinfoil must be left remaining upon the scale during the experiment); both scales are then equally loaded, say with about fifty grammes each, and, if necessary, the balance is again adjusted (by the addition of small weights, &c.) The load of the two scales is then interchanged, so as to transfer that of the right scale to the left, and *vice versâ*. A balance with perfectly equal arms must maintain its absolute equilibrium upon this interchange of the weights of the two scales.

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or substance has to be weighed repeatedly, the weights may be left on the scale without risk to the balance. We find it now in almost all delicate balances. Single stops fixing both beam and scales by one and the same act (by a turn), appear to me less practical, as the fixing of the scales upon every fresh addition of a small weight, whilst answering no rational purpose, occupies a good deal of time, which might be more profitably employed.

4. The balance is accurately adjusted; it is then arrested, subsequently set in motion, and again allowed to recover its equilibrium; the same process should be repeated several times. A good balance must invariably re-assume its original equilibrium. A balance of which the end edges afford too much play to the hook resting upon them, so as to allow the latter slightly to alter its position, will show perceptible differences in different trials. This fault, however, is possible only with balances of defective construction.

A balance to be practically useful for the purposes of quantitative analysis *must* stand the first, second, and last of these tests. A slight inequality of the arms is of no great consequence, since this may be readily and completely remedied by the manner of weighing.

As the sensibility of a balance will speedily decrease if the steel edges are allowed to get tarnished by oxidation, delicate balances should never be kept in the laboratory, but always in a separate room. It is also advisable to place within the case of the balance a vessel half filled with calcined carbonate of potassa, to keep the air dry. I think I need hardly add that this salt must be re-calcined whenever it has absorbed moisture.

§ 8.

b. The Weights.

1. The French gramme is the best standard for calculation. A set of weights ranging from fifty grammes to one milligramme may be considered sufficient for all practical purposes. With regard to the set of weights, it is generally a matter of indifference in chemical experiments whether the gramme, its multiples and fractions, are really and perfectly equal to the accurately adjusted *normal* weights of the corresponding denominations;* but it is *absolutely* and *indispensably necessary* that they should agree *perfectly* among and with each other, *i.e.*, the $\frac{1}{100}$ gramme weight must be exactly the one hundredth part of the gramme weight of the set, &c. &c.

2. The whole of the set of weights should be kept in a suitable, well-closing box; and it is desirable likewise that a distinct compartment be appropriated to every one even of the smaller weights.

3. As to the shape best adapted for weights, I think that of short cylinders, with a handle at the top, the most convenient and practical form for the large weights; small square pieces of platinum foil, turned up at one corner, are best adapted for the minute and fractional weights. The foil used for this purpose should not be too thin, and the respective compartments adapted for the reception of the several smaller weights in the box, should be large enough to admit of their contents being taken out of them with facility, or else the smaller weights will soon get cracked, bruised, and indistinct. Every one of the weights (with the exception of the milligramme),† should be distinctly marked.

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* Still it would be desirable that mechanicians who make gramme-weights intended for the use of the chemist, should endeavor to procure *normal* weights. It is very inconvenient, in many cases, to find notable differences between weights of the same denomination, but coming from different makers; as I myself have often had occasion to discover.

† Milligramme = ·0154 grains Troy.
Centigramme = ·1543 ,, ,,
Decigramme = 1 5434 ,, ,,
Gramme = 15·4346 ,, ,,

4. With respect to the material most suitable for the manufacture of weights, I think that, although rock crystal is admirably adapted for normal weights, its high price, and the inconvenient form of the pieces, render it far less so for weights intended to serve in the processes of quantitative analysis. Platinum weights would be sure to be universally adopted, were the metal not too expensive; but as it is, we commonly rest satisfied with having the smaller weights only, from one gramme downwards, made of platinum foil, using brass weights for all the higher denominations. Brass weights must be carefully shielded from the contact of acid or other vapors, or their correctness will be impaired; nor should they ever be touched with the fingers, but always with small pincers. But it is an erroneous notion to suppose that weights slightly tarnished are unfit for use. It is, indeed, hardly possible to prevent weights for any very great length of time from getting slightly tarnished. I have carefully examined many weights of this description, and have found them as exactly corresponding with one another in their relative proportions as they were when first used. The tarnishing coat, or incrustation, is in most instances so extremely thin, that even a very delicate balance will generally fail to point out any perceptible difference in the weight. It will, however, be found very advantageous to gild the brass weights (by the electro-galvanic process) previously to adjusting them.

The exact accordance and agreement of the several denominations of weights of the same set may be fully tested and assayed in the following manner :—

One scale of a very delicate balance is loaded with a one-gramme* weight, and the balance is then completely equipoised by placing an exactly equivalent weight in small pieces of brass, and finally tinfoil (not paper, since this absorbs moisture), upon the other scale. The weight is then removed, and replaced successively by the other gramme weights which the operator may happen to possess, and afterwards by the same amount of weight in pieces of lower denominations.

The balance is carefully scrutinized at every fresh assay, and any deviation from the exact equilibrium marked. The several pieces of higher denominations are then tested, and assayed in the same way. In the comparison of the smaller with the larger weights, the former must not show the slightest perceptible difference on a balance turning with $\frac{1}{10}$ of a milligramme; differences, however, of from the $\frac{1}{10}$ to $\frac{2}{10}$ part of a milligramme may be passed over in the larger weights, since this will not materially impair their usefulness. If you wish them to be more accurate, you must adjust them yourself. In the purchase of weights chemists ought always to bear in mind that an accurate weight is truly valuable, whilst an inaccurate one is absolutely worthless. Experience has taught me that it is invariably the safest way for the analytical chemist to test every weight he purchases, no matter how high the reputation of the maker may happen to stand.

§ 9.

c. THE PROCESS OF WEIGHING.

We have two different methods of determining the weight of substances; the one is termed "*direct weighing*," the other is called "*weighing by substitution*."

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* Gramme = 15·4346 grains Troy.

In *direct weighing*, the substance is placed upon one scale, and the weight upon the other. If we possess a balance, the arms of which are of equal length, and the scales in a perfect state of equilibrium, it is indifferent upon which scale the substance is placed in the several weighings required during an analytical process; *i.e.*, we may weigh upon the right or upon the left side, and change sides at pleasure, without endangering the accuracy of our results. But if, on the contrary, the arms of our balance are not perfectly equal, or if the scales are not in a state of perfect equilibrium, we are compelled to weigh invariably upon the same scale, otherwise the correctness of our results will be more or less materially impaired.

Suppose we want to weigh one gramme of a substance, and to divide this amount subsequently into two equal parts. Let us assume our balance to be in a state of perfect equilibrium, but with unequal arms, the left being 99 millimetres,* the right 100 millimetres long; we place a gramme weight upon the left scale, and against this, on the right scale, as much of the substance to be weighed as will restore the equilibrium of the balance.

According to the axiom, "masses are in equilibrium upon the lever, if the distance of their products from the point of support is equal," we have consequently upon the right scale 0·99 grm. of substance, since 99 : 1·00 = 100 : 0·99. If we now, for the purpose of weighing one half the quantity, remove the whole weight from the left scale, substituting a 0·5 grm. weight for it, and then take off part of the substance from the right scale, until the balance recovers its equilibrium, there will remain 0·495 grm.; and this is exactly the amount we have removed from the scale: we have consequently accomplished our object with respect to the relative weight; and, as we have already remarked, the absolute weight is not generally of so much importance in chemical experiments. But if we attempted to halve the substance which we have on the right scale, by first removing both the weight and the substance from the scales, and placing subsequently a 0·5 grm. weight upon the *right* scale, and part of the substance upon the *left*, until the balance recovers its equilibrium, we should have 0·505 of substance upon the left scale, since 100 : 0·500 = 99 : 0·505; and consequently, instead of exact halves, we should have one part of the substance amounting to 0·505, the other only to 0·495.

If the scales of our balance are not in a state of absolute equilibrium, we are obliged to weigh our substances in vessels (see § 10, 5), to ensure accurate results (although the arms of the balance be perfectly equal). It is self-evident that the weights in this case must likewise be invariably placed upon one and the same scale, and that the difference between the two scales must not undergo the slightest variation during the whole course of a series of experiments.

From these remarks result the two following rules:—

1. It is, under all circumstances, advisable to weigh substances invariably upon one and the same scale.

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* Millimetre = ·03937 inch.
Centimetre = ·3937 inch.
Decimetre = 3·937 inches.
Metre . . = 39·37 inches.

2. If the operator happens to possess a balance for his own private and *exclusive* use, there is no need that he should adjust it at the commencement of every analysis; but if the balance be used in common by several persons, it is absolutely necessary to ascertain, before every operation, whether its state of absolute equilibrium may not have been disturbed.

Weighing by substitution yields not only *relatively*, but also *absolutely* accurate results; no matter whether the arms of the balance be of exactly equal lengths or not, or whether the scales be in perfect equipoise or not.

The process is conducted as follows: the substance to be weighed—say a platinum crucible—is placed upon one scale, and the other scale is accurately counterpoised against it. The platinum crucible is then removed, and the equilibrium of the balance restored by substituting weights for the removed crucible. It is perfectly obvious that the substituted weights will invariably express the real weight of the crucible with absolute accuracy. We weigh by substitution whenever we wish to obtain *absolutely* accurate results; as, for instance, in the determination of atomic weights. The process may be materially shortened by accurately determining and noting, in the first place, the weight of a certain tare intended to serve as a counterpoise, and which must, of course, be heavier than the substance (or substances) we wish to weigh; this tare, or counterpoise is then shifted to the opposite scale, and the substance to be weighed placed on the other, together with the smaller weights requisite to restore the equilibrium of the balance. The sum of the weights added is then subtracted from the known amount of the counterpoise: the remainder will at once indicate the exact weight of the substance we are dealing with. Let us suppose, for instance, we have on the left scale a tare requiring on the right a weight of exactly fifty grammes to counterpoise it; we shift the tare to the right scale, and place on the left, say a platinum crucible. We find that it requires an addition of weight to the extent of 10 grammes to counterpoise the tare on the right scale. Accordingly, the crucible weighs 50 grammes *minus* 10 = 40 grammes.

§ 10.

The following rules will be found useful in performing the process of weighing:—

1. The safest and most expeditious way of ascertaining the exact weight of a substance, is to avoid trying weights at random; instead of this, a strictly systematic course ought to be pursued in counterpoising substances on the balance. Suppose, for instance, we want to weigh a crucible, the weight of which subsequently turns out to be 6·627 grammes; well, we place 10 grammes on the other scale against it, and we find this is too much; we place the weight next in succession, *i.e.*, 5 grammes, and find this too little; next 7, too much; 6, too little; 6·5, too little; 6·7, too much; 6·6, too little; 6·65, too much; 6·62, too little; 6·63, too much; 6·625, too little; 6·627, right.

I have selected here, for the sake of illustration, a most complicated case; but I can assure the student of quantitative analysis that this systematic way of trying the counterpoising of substances will in most instances lead to the desired end, in half the time required where weights are tried at random. A few minutes will generally suffice to ascertain the weight of a substance to within the $\frac{1}{10}$ of a milligramme.

2. I have already had occasion to observe that the placing of small riders, or hooks, weighing one centigramme each, on or between the points of the decimal divisions of the beam, is a more expeditious way to determine a milligramme, and its decimal divisions, than the use of the corresponding weights upon the scale.

3. Particular care and attention should be bestowed on entering the weights on paper. The best way is to put down the weights first by inference from the blanks, or gaps in the weight box, and to control and verify the notation subsequently by removing the weights from the scale, and replacing them in their respective compartments in the box. The student should from the commencement make it a rule to enter the number to be deducted in the *lower line*. Thus, in the upper line, the weight of the crucible + the substance; in the lower line, the weight of the empty crucible.

4. The balance ought to be arrested every time any change is contemplated, such as removing weights, substituting one weight for another, &c. &c., or it will soon get spoiled.

5. Substances (except, perhaps, pieces of metal, or some other body of the kind) must never be placed *directly* upon the scales, but ought to be weighed in appropriate vessels of platinum, silver, glass, porcelain, &c. &c., never in paper or card, since these, being liable to attract moisture, are apt to alter in weight. The most common method is to weigh in the first instance the vessel by itself, and to introduce subsequently the substance into it; to weigh again, and subtract the former weight from the latter. In many instances, and more especially where several portions of the same substance are to be weighed, the united weight of the vessel and of its contents is first ascertained; a portion of the contents is then taken out, and the vessel weighed again; the difference between the latter and the original weight expresses the amount of the portion taken out of the vessel.

6. Substances liable to attract moisture from the air, must be weighed invariably in closed vessels (in covered crucibles, for instance, or between two watch glasses, or in a closed glass tube); fluids are to be weighed in small bottles closed with glass stoppers.

7. A vessel ought never to be weighed whilst hot, since it will in that case invariably weigh lighter than it really is. This is owing to two circumstances. In the first place, every body condenses upon its surface a certain amount of air and moisture, the quantity of which depends upon the temperature and the hygroscopic state of the air, and likewise on its own temperature. Now suppose a crucible has been weighed cold at the commencement of the operation, and is subsequently weighed again whilst hot, together with the substance it contains, and the weight of which we wish to determine. If we subtract for this purpose the weight of the cold crucible, ascertained in the former instance, from the weight found in the latter, we shall subtract too much, and consequently we shall set down less than the real weight for the substance. In the second place, bodies at a high temperature are constantly communicating heat to the air immediately around them; the heated air expands and ascends, and the denser and colder air, flowing towards the space which the former leaves, produces a current which tends to raise the scale, making it thus appear lighter than it really is.

8. If we suspend from the end edges of a correct balance respectively 10 grammes of platinum and 10 grammes of glass, by wires of equal weight, the balance will assume a state of equilibrium; but if we subsequently immerse the platinum and glass completely in water, this equilibrium will at once cease, owing to the different specific gravity of the two substances; since, as is well known, substances immersed in water lose of their weight a quantity precisely equal to the weight of their own bulk of water. If this be borne in mind, it must be obvious to every one that weighing in the air is likewise defective, inasmuch as the bulk of the substance weighed is not the same with that of the weight. This defect, however, is so very insignificant, owing to the trifling specific gravity of the air in proportion to solid substances, that we may generally disregard it altogether in analytical experiments. In cases, however, where *absolutely* accurate results are required, the bulk both of the substance examined, and of the weight, must be taken into account, and the weight of the corresponding volume of air added respectively to that of the substance and of the weight, making thus the process equivalent to weighing *in vacuo*.

§ 11.

2. Measuring.

The process of measuring is confined in analytical researches mostly to gases and fluids. The method of measuring gases has been lately so greatly improved by Bunsen, and by Regnault and Reiset, that it may be said to equal in accuracy the method of weighing. However, such accurate measurement of gases demand an expenditure of time and care, such as can be bestowed only on the nicest and most delicate scientific investigations.*

The measuring of fluids in analytical investigations was resorted to first by *Descroizilles* ("Alkalimeter," 1806). *Gay-Lussac* has materially improved, and it may almost be said, *perfected* the process (measuring of the solution of chloride of sodium used in the assay of silver in the humid way). More recently *F. Mohr*† has bestowed much care and ingenuity upon the production of appropriate and convenient measuring apparatus, and has added to our store the eminently practical *compression stop-cock burette*. Still, however so much the method of measuring fluids has been perfected, yet it can never be expected to attain to the accuracy of weighing. But, as the inaccuracies inherent in the method may, in most cases, be reduced to the most harmless proportions by appropriate dilution of the fluid to be measured, the process is now resorted to even in most accurate scientific investigations; since it requires much less time than the process of weighing.

The accuracy of the results obtained by measuring depends upon the proper construction of the measuring apparatus, and also upon the manner in which the process is conducted.

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* For a detailed description of *Bunsen's* method, I refer the student to the article on the "Eudiometer," by *H. Kolbe*, in *Liebig*, *Poggendorff*, and *Wöhler's* "Handwörterbuch der Chemie," ii. 1053, and vol. i. 2nd edition, 930, (art. "Analysis, volumetrical, for Gases," by *Kolbe* and *Frankland*; and also the "Gasometrical Methods," by *Robert Bunsen*, translated by Roscoe. Most useful and valuable information may be derived from the latter work, by all who wish to occupy themselves with the analysis of gases.

† "Lehrbuch der Titrirmethode," by Dr. *F. Mohr*. Brunswick, 1855.

§ 12.

a. THE MEASURING OF GASES.

We use for the measuring of gases graduated tubes of greater or less capacity, made of strong glass, and closed by fusion at one end, which should be rounded. The following apparatus will be found sufficient for all the processes of gas measuring required in organic elementary analyses.

1. A bell-glass capable of holding from 150 to 250 cub. cent.,[*] and about 4 centimetres in diameter; this bell-glass should be graduated into cubic centimetres.

2. From five to six glass tubes, about 12 to 15 millimetres in diameter in the clear, and capable of holding from 30 to 40 cub. cent. each, divided into double cub. millim., so that every line corresponds to 2 cub. millim. The sides of these tubes should be pretty thick, otherwise they will be liable to break, especially when used to measure over mercury. The sides of the bell-glass should be from 4 to 6, those of the tubes from 2 to 3 millimetres thick.

The most important point, however, is that the tubes be correctly graduated, since upon this of course depends the accuracy of the results.[†]

The practical usefulness of the measuring tubes depends principally upon the fulfilment of three conditions.

1. The divisions of the tube must exactly correspond with each other.

2. The divisions of every one of the tubes must exactly correspond with those of the other tubes. And,

3. The volumes marked on the graduation line must exactly correspond with the weights used by the analyst.

The following experiments serve to test our gas-measuring tubes.

a. The tube which it is intended to examine is placed in a perpendicular position, and filled gradually with accurately measured small quantities of mercury, care being taken to ascertain with the utmost accuracy and precision whether the graduation of the tube is proportionate to the equal volumes of mercury poured in. The measuring of the mercury is effected by means of a small glass tube closed (by fusion) at one end, and ground perfectly even and smooth at the other. This tube is filled to overflowing by immersion under mercury, care being taken to allow no air bubbles to remain in it; the excess of mercury is then removed by pressing a small glass plate down on the smooth edge of the tube.[‡]

b. Different quantities of mercury are measured off in one of the smaller tubes, and then successively transferred into the other tubes. The tubes may be considered in perfect accordance with each other, if the mercury reaches invariably the same divisional point in every one of them.

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[*] Cubic centimetre = ·0610 cubic inch.

[†] For the manner of graduating the tubes, the student may consult *Berzelius*' "Manual of Chemistry," 4th edition, vol. x., article "Measuring;" or *Williams*' "Chemical Manipulations;" or the article on the "Eudiometer," in *Liebig*, *Wöhler*, and *Poggendorff's* "Handwörterbuch der Chemie."

[‡] As warming the metal is to be carefully avoided in this process, it is advisable not to hold the tube with the finger and thumb, in immersing it in the mercury, but to fasten it in a small wooden holder.

Such tubes as are intended simply to determine the relative volume of different gases, need only correspond individually and collectively in the divisions of their graduated scales; but in cases where we want to calculate the *weight* of a gas by inference from its *volume*, it is necessary also to ascertain whether the volumes indicated by the degrees of the graduation scale correspond with the weights in our possession.

c. For this purpose one of the tubes is accurately weighed and then filled with distilled water of a temperature of 60·8° Fah. to the last mark of the graduated scale; the weight of the water is then accurately determined. If the tubes agree with the weight, every 100 cub. cent. of water of 60·8° Fah. must weigh 99·9° grammes. But should it happen that the accordance between the divisions of the tubes and the weights of the balance be not so perfect, no matter whether the error lie in the graduation of the tube or in the adjustment of the weights, we cannot proceed at once to calculate the weight of a gas from its ascertained volume, but have, in the first place, to reduce the latter in proportion to the difference existing between the divisions of our graduated scales and our weights. Let us suppose, for instance, that, upon examining our measuring tubes, we find 100 cub. cent. of water, as indicated by the scale of the tubes, to weigh only 99·6 grammes: assuming our weights to be correct, the cubic centimetres of our scale are accordingly too small; and if we therefore wish to convert the measured volume of a gas, as ascertained by our scale, into weight, we must, in the first place, convert the cub. cent. of our scale into normal cubic centimetres.

$$99{\cdot}9 : 99{\cdot}6 :: 100 : x.$$

In the *analysis of gaseous bodies* by Bunsen's methods (which are the simplest and most accurate) the use of a suitable eudiometer is indispensable. *Bunsen's* eudiometer (see Fig. 1) consists of a glass tube from 500 to 600 millimetres long, having an internal diameter of about 19 millimetres, and as far as practicable of uniform calibre throughout, the glass not above 1¼ mm. thick. At the upper closed end two pieces of fine platinum wire are melted into the glass in opposite points; the inner ends of these wires are clinched down close to the side of the glass, approaching each other at the apex of the eudiometer to within 3 millimetres.

The tube is graduated into millimetrical divisions by means of a very ingeniously constructed divider. The volumes corresponding to the respective divisional lines are subsequently determined by measuring into the tube equal volumes of mercury. The corresponding volumes are noted down in a table. This mode of graduating and adjusting measuring tubes is unquestionably the best.

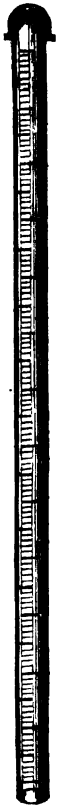

Fig. 1.

Besides this instrument, another shorter measuring tube is required, also graduated into millimetrical divisions. The tube is slightly curved at the lower end, as shown in Fig 2.

Its length is 250 mm., its inner diameter 19 mm.; the glass of which it is made is 2 mm. thick.

In the measuring of gases we must have regard to the following points:—

1. We must endeavor to determine as accurately as possible the exact height at which the water or mercury stands. 2. We must take into consideration the temperature of the gas. 3. The degree of pressure operating upon it. And 4. The circumstance whether it is dry or moist. The three latter points will be readily understood, if it be borne in mind that any alteration in the temperature of gases, or in the pressure acting upon them, or in the tension of the admixed aqueous vapor, involves likewise a considerable alteration in their respective volumes.

Fig. 2.

§ 13.

Ad. 1. CORRECT READING-OFF.

With regard to the first point, it is somewhat difficult to decide with absolute accuracy the exact degree of the scale at which the mercury or water may happen to stand in the gasometer, since mercury in a jar or cylinder (more especially in a narrow one), has a convex surface, owing to its own cohesion; whilst water, on the other hand, under the same circumstances has a concave surface, owing to the attraction which the walls of the tube exercise upon it. To ascertain the exact position of the mercury or water, the jar or cylinder should invariably be placed in a perfectly perpendicular position, and the eye of the operator brought to a level with the surface of the fluid. The perpendicular position of the cylinder may be readily adjusted by means of two plummets suspended at a short distance from the cylinder, and at a proper distance from each other. To bring the eye to an exact level with the surface of the fluid in the cylinder, a small mirror is pressed firmly against the tube, on the opposite side, and the centre of the eye fixed on the mirror right across the surface of the fluid. When the eye is thus placed in the right position, the mirror is removed, and the exact height of the fluid read off.

Bunsen also substitutes for the mirror a telescope placed horizontally at a distance of from four to six paces from the eudiometer, and movable in a vertical direction. This arrangement, besides greatly facilitating the reading-off, affords, also, in the measuring of gases, this additional great advantage, that, as the observer is placed at a greater distance from the measuring tube, expansion of the gas from his close vicinity to the tube need not be apprehended as in reading-off with the aid of the mirror. (*Kolbe*). If water is used as the confining fluid, the middle of the dark zone formed by that liquid around the inner walls of the tube, in obedience to the attraction exercised upon it by these walls, is assumed to be the real surface; whilst when operating with mercury, we have to place the real surface in a line drawn exactly in the centre between the highest point of the surface of the mercury, and the points at which the latter is in actual contact with the walls of the tube. However, the results obtained in this way are only approximate. Absolutely accurate results cannot be arrived at, in measuring over water or any other fluid that adheres to glass. But over mercury they may be arrived at. To this end, it is simply requisite to determine the error of the meniscus. This is done for each respective tube, once for all, in the following manner: a certain amount of mercury is poured into the tube, and its height read off right on a level with the top of the convex surface exhibited by it; a few drops of solution of chloride of mercury are then poured on the top of the metal; this causes the convexity to disappear; the height of the mercury in the tube is now read off again: the difference between the two readings is the error of the meniscus. In the process of graduation, the tube stands upright, in that of measuring gases, it is placed upside down; the error of the meniscus must accordingly be doubled, and the sum added to each volume of gas read off over the top of the convex surface of the mercury. (*Kolbe.*)

The mercury intended to serve in the measuring of gases should be pure; it must, more particularly, be free from lead and tin, since an admixture of either of these metals imparts to mercury the property of adhering to glass. Should lead or tin happen to be present, it may be removed by keeping the mercury in contact for a day with dilute nitric acid in a shallow basin, taking care to stir frequently. From dust, &c., mercury may be freed by filtration through a cloth.

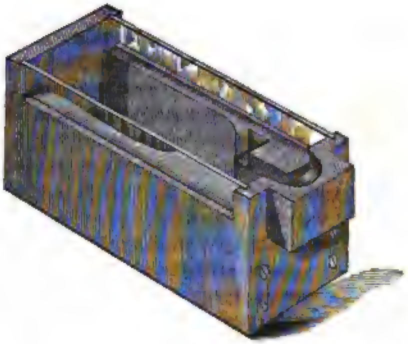

Fig. 3.

The process of collecting and measuring gases requires the aid of a pneumatic trough;—the one constructed by Bunsen, which is represented in Fig. 3, is very practical; it consists of strong wood, and is either cut and fashioned out of the solid block, or constructed of thick boards closely joined and screwed together. It is 33 centimetres long, 13·5 cent. broad, and 17 cent. deep. The upper parts of the long lateral sides are replaced by strips of strong glass set into the wood; in this way a rectangular chamber is formed at the top, enclosed on the long sides by glass, on the short sides by wood. This chamber, which is 30 cent. long, 11·5 broad, and 3 deep, is provided in front with an outlet; it extends downwards into a cavity, chiselled out of the wood, which is 7 cent. wide behind, but only 2·5 cent. in the fore part; as this cavity accordingly gets gradually narrower towards the fore part, so its depth also decreases, being 10 cent. behind, and only 8 cent. in front (measured from the uppermost top of the trough). In the narrower part of this cavity, or well, the wall does not ascend uniform in width up to the top, but 24 mm. from the bottom there is a break, or landing, the walls from this point upwards receding at a right angle, which gives to the channel, from this part to the top, a breadth of 36 mm. By this disposition of the walls, firm shelves are formed on both sides, 70 mm. long, and 6 mm. broad, on which the tubes may be supported during the operation of inserting into their lower orifice a ball, &c. Similar shelves are chiselled out of the wood also on the sides of the channel. The glass strips facilitate the reading off deep mercury levels.

Lastly, in order to enable the operator to accurately determine the volume of a gas collected over mercury, it is above all indispensable, previously to the introduction of the gas, to fill the cylinder first completely with mercury, taking due care to exclude all air-bubbles. *Bunsen* has taught us to attain this object in a simple way, by pouring the mercury into the perfectly clean and dry tube through a funnel having attached to its neck, by means of a cork (or india-rubber), a narrow glass tube of the same length as the measuring cylinder.

§ 14.

Ad. 2. INFLUENCE OF TEMPERATURE.

The temperature of gases to be measured is determined either by making it correspond with that of the confining fluid, and ascertaining the latter, or by suspending a delicate thermometer by the side of the gas to be measured, and noting the degree which it indicates.

If the construction of the pneumatic apparatus permits the total immersion of the cylinder in the confining fluid, a corresponding temperature between the latter and the gas which it is intended to measure, is most readily and speedily obtained; but in the reverse case, the operator must always, after every manipulation, allow half an hour or, in operations combined with application of heat, even an entire hour to elapse, before proceeding to observe the state of the mercury in the cylinder, or jar, and in the thermometer.

Proper care must also be taken, after the temperature of the gas has been duly adjusted, to prevent re-expansion during the reading-off; all injurious influences in this respect must accordingly be carefully guarded against, and the operator should, more especially, avoid laying hold of the tube with his hand (in pressing it down, for instance, into the confining fluid); but he should, in this and similar operations, make use of small wooden pincers or of a clothes-peg.

As, on account of the necessity of the most perfect correspondence being always maintained between the temperature of the gas and that of the surrounding air, every sudden change of temperature would necessarily prove prejudicial to the accuracy of the results, it is always advisable to select for the performance of analyses of gases a properly sheltered room with northern aspect.

§ 15.

Ad. 3. INFLUENCE OF PRESSURE.

With regard to the third point, the gas is under the actual pressure of the atmosphere if the confining fluid stands on an exact level both in and outside the cylinder; the degree of pressure exerted upon it may therefore at once be ascertained by consulting the barometer. But if the confining fluid stands *higher* in the cylinder than outside, the gas is under *less* pressure,—if *lower*, it is under *greater* pressure than that of the atmosphere; in the latter case, the perfect level of the fluid inside and outside the cylinder may readily be restored by raising the tube; if the fluid stands higher in the cylinder than outside, the level may be restored by depressing the tube; this however can only be done in cases where we have a trough of sufficient depth. When operating over water, the level may in most cases be readily effected; when operating over mercury, it is, more especially with wide tubes, often impossible to bring the fluid to a perfect level inside and outside the cylinder.

In the case illustrated in Fig. 4, we have the gas under the pressure of the atmosphere, *minus* the pressure of a column of mercury equal in length to the line *a b*. This pressure may be determined, therefore, by measuring the length of *a b* with the greatest possible accuracy, and subtracting it from the actual state of the barometer. Suppose, for instance, the barometer stands at 758 mm., and the length of *a b* is = 100 mm., the actual pressure upon the gas will be 758 – 100 = 658 mm. mercury.

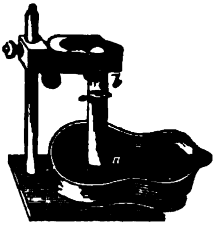

Fig. 4.

If we have water, or some other fluid (solution of potassa, for instance), over the mercury, we proceed generally as if this were not the case; *i. e.*, we either place the mercury on a level inside and outside the cylinder, or measure the difference between the surface of mercury in the cylinder and that in the trough. The pressure of the column of water, &c. &c., floating over the mercury, is mostly so trifling that it may safely be disregarded altogether. The more correct way, of course, would be to measure the height of the column of water, &c., to reduce this upon mercury, and to subtract the result from the actual state of the barometer. But this correction may usually be omitted, since, as has already been stated, absolutely correct results cannot be arrived at under such circumstances.

§ 16.

Ad. 4. INFLUENCE OF MOISTURE.

In measuring gases saturated with aqueous vapor, it must be taken into account that the vapor, by virtue of its tension, exerts a pressure upon the confining fluid; the result must, therefore, be corrected accordingly. This is an easy task, however, since we know the respective tension of aqueous vapor for the various degrees of temperature. To this end it is, of course, necessary that the gas should be actually saturated with the vapor. It is, therefore, indispensable in measuring gases to take care either to have the gas absolutely dry, or thoroughly saturated with aqueous vapor.

The drying of gases confined over mercury is effected by means of a ball of fused chloride of calcium, stuck on a platinum wire; this is prepared by inserting the wire, bent at the lower end in form of a hook, into a pistol-bullet mould of about 6 mm. inner diameter, and then filling the hollow with chloride of calcium heated just to the fusing point; the chloride of calcium used must be free from caustic lime. The neck sticking to the ball is, after cooling, removed with a knife. When it is intended to dry a gas, this ball is, with the aid of the wire, pushed through the mercury, and inserted into the orifice of the cylinder containing the gas; after having been left there for the space of an hour or so, the ball is withdrawn, the gas being now perfectly dry. Whilst the ball remains within the cylinder, the end of the wire must be kept below the surface of the mercury in the trough, since otherwise we should inevitably have diffusion of the confined gas and the outer air, at that part of the wire which is not covered by the mercury.

Where it can be done, it will always be found more convenient to saturate gases with moisture before measuring them. *Bunsen* effects this object by introducing an iron wire, with a droplet of water the size of a pin's head adhering to it, into the empty measuring cylinder and casting the water off in the top, without wetting any other portion of the tube. The quantity of water thus introduced in the cylinder is more than sufficient, at the common temperature, to saturate with aqueous vapor the gas subsequently passed into the cylinder.

It is quite obvious from the preceding remarks, that volumes of different gases can be compared only if measured at the same temperature, under the same pressure, and in the same hygroscopic state. The temperature is generally reduced to 32° F., the hygroscopic state of the gases to 0, and the pressure to 0·76 met. barometer. How this is effected, as well as the manner in which we deduce the weight of gases from their bulk, will be found in the chapter on the calculation of analyses.

§ 17.

b. The Measuring of Fluids.

In consequence of the vast development which volumetrical analysis has of late acquired, the measuring of fluids has become an operation of very frequent occurrence in analytical researches. According to the different objects in view, various kinds of measuring vessels are employed. The number of vessels proposed or suggested for the measuring of fluids in volumetrical processes has indeed now increased to such an extent, that I must forbear discussing all the forms and dispositions recommended, and simply confine myself to the description of such measuring apparatus as I have found the most practical and convenient in my own laboratory.

Before entering into details, I have to observe that the operator must, in the case of every measuring vessel, carefully distinguish whether the vessel is graduated for *holding* or for *delivering* the exact number of cubic centimetres marked on it. If you have made use of a vessel of the former description in measuring off 100 cub. cent. of a fluid, and wish to transfer the latter completely to another vessel, you must, after emptying your measuring vessel, rinse it, and add the rinsing to the fluid transferred; whereas, if you have made use of a measuring vessel of the latter description, there must be no rinsing.

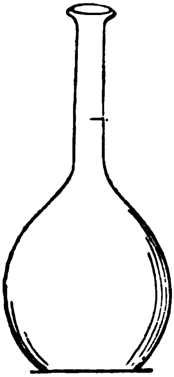

Fig. 5.

a. Measuring vessels graduated for holding the exact measure of fluid marked on them.

aa. Measuring vessels which serve to measure out definite quantities of fluid.

We use for this purpose—

§ 18.

1. *Measuring Flasks.*

Fig. 5 represents a measuring flask of the most practical and convenient form.

Measuring flasks of various sizes are sold in the shops, holding respectively 200, 250, 500, 1000, 2000, &c., cub. cent. As a general rule, they have no ground-glass stoppers; it is, however, very desirable, in certain cases, to have measuring flasks with ground stoppers. The flasks must be made of well-annealed glass of uniform thickness, so that fluids may be heated in them. The line-mark should be placed within the lower third or, at least, within the lower half-division of the neck.

Measuring flasks, before they can properly be employed in analytical operations, must first be carefully tested to determine their exact capacity. The best and simplest way of effecting this is to proceed thus:—Put the flask, perfectly dry inside and outside, on the one scale of a sufficiently delicate balance, together with a weight of 1000 grammes in the case of a litre flask, 500 grammes in the case of a half-litre flask, &c., restore the equilibrium by placing the requisite quantity of shot and tinfoil on the other scale, then remove the flask and the weight from the scale on which they are placed (leaving, of course, the shot and tinfoil on the other scale), put the flask on a perfectly level table or shelf, and in that position pour in distilled water of 60·8° F.,* until the lower border of the dark zone formed by the surface stratum of the water around the inner walls is on an exact level with the line-mark. After having thoroughly dried the neck of the flask above the mark, replace the flask upon the scale: if this restores the perfect equilibrium of the balance, the water in the flask weighs, in the case of a litre measure, exactly 1000 grammes, in the case of a half-litre measure, exactly 500 grammes, &c. If the scale bearing the flask sinks, the water in it weighs as much above 1000 grammes, &c., as the additional weights amount to which you have to put in the other scale to restore the equilibrium; if it rises, on the other hand, the water weighs as much less as the weights amount to which you have to put in the scale with the flask to effect the same end.

If the water in the litre-measure weighs 999 grammes,† in the half-litre measure, 499·5 grammes, &c., the measuring flasks are correct. Differences up to 0·100 grm. in the litre-measure, up to 0·070 grm. in the half-litre measure, and up to 0·050 grm. in the quarter-litre measure, are not taken into account, as one and the same measuring flask will in repeated consecutive weighings, though filled each time exactly up to the mark, with water of the same temperature, be found to differ within these limits.

Though a flask should, upon examination, turn out not to hold the exact quantity of water which it is stated to contain, it may yet possibly agree with the other measuring vessels, and may accordingly still be perfectly fit for use for most purposes. Measuring vessels agree among them if the number of cubic centimetres marked upon them severally bears in all of them respectively the same relative proportion to the ascertained weight of the water; thus, for instance, supposing your litre-measure to hold 998 grammes of water of 60·8° F., and your pipette of 50 cub. cent. nominal capacity, to *give* 49·9 grammes of water of the same temperature, the two measures agree, since

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* To use water in the state of its highest density, viz., of 39·2 F., 1 cub. cent. of which weighs exactly 1 grm., and, accordingly, 1 litre, exactly 1000 grammes, is less practical, as the operations must in that case be conducted in a room of the same temperature; since, in a warmer room, the outside of the flask would immediately become covered with moisture, in consequence of the air cooling below dew-point. Nor can I recommend *F. Mohr's* suggestion to make litre flasks, and measuring vessels in general, upon a plan to make the litre flask, for instance, hold, not 1000 grammes of 39·2 F., but 1000 grammes of 63·5 F., since in an arrangement of the kind proper regard is not paid to the actual purport and meaning attached to the term "litre" in the scientific world; and measuring-vessels of the same recognised capacity, made by different instrument-makers, are thus liable to differ to a greater or less extent. One litre-flask, according to *Mohr*, holds 1001·2 standard cub. cent. I consider it impractical to give to the cub. cent. another signification in vessels intended for measuring fluids than in vessels used for the measuring of gases, which latter demand strict adhesion to the standard cub. cent., as, in the analysis of gaseous bodies, it is often required to deduce the weight of a gas by calculating from the volume.

† With absolute accuracy, 998·981 grammes.

$$1000 : 50 :: 998 : 49{\cdot}9.$$

To prepare or correct a measuring flask for use, counterpoise the dry-litre- half-litre- or quarter-litre-flask most accurately, and then weigh into it, by substitution (§ 9), 999 grammes, or, as the case may be, the one-half or one-fourth of that quantity of distilled water of 60·8° F. Put the flask on a perfectly level table or shelf, place your eye on an exact level with the surface of the water, and mark the lower border of the dark zone by two little dots made on the glass with a point dipped into thick asphaltum varnish, or some other substance of the kind. Now pour out the water, place the flask in a convenient position, and cut with a diamond a fine distinct line into the glass from one dot to the other.

Measuring flasks are occasionally also graduated for *delivering* the exact number of cubic centimetres of their nominal capacity; these, however, can properly be used only in operations where minute accuracy is not absolutely indispensable, since the water-drops which remain adhering to the glass inside the flask vary not inconsiderably in number and bulk, which may give rise to perceptible differences in the results of several measurements with one and the same flask. If you wish to graduate a flask for delivering, or to test one so graduated, pour water into it, empty it again, let it drain, and then weigh into it the exact weight of distilled water of 60·8° F. corresponding to the number of cub. cent. which the flask is stated to hold.

bb. Measuring vessels which serve to measure out indefinite quantities of fluid.

§ 19.

2. *The Graduated Cylinder.*

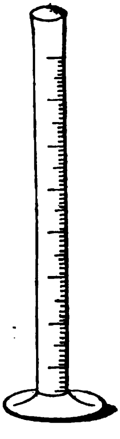

Fig. 6.

This instrument, represented in Fig. 6, should be about 3 centimetres wide, of a capacity of 300 cub. cent., and graduated into cub. cent. It must be ground level at the top, that it may be covered quite close with a ground glass plate. The measuring with cylinders is not quite so accurate as with measuring flasks, as in the latter the volume is read off in a narrower part. The accuracy of measuring cylinders may be tested in the same way as in the case of measuring flasks, viz., by weighing into them water of 60·8° F.; or, also equally well, by letting certain definite quantities of fluid flow into the cylinder from a correct pipette or burette graduated for delivering, and observing whether or not the quantity is correctly indicated by the scale of the cylinder.

β. MEASURING VESSELS GRADUATED FOR DELIVERING THE EXACT MEASURE OF FLUID MARKED ON THEM (Measuring vessel graduated *à l'écoulement*).

aa. Measuring vessels which serve to measure out definite quantities of fluid.

§ 20.

3. *The Graduated Pipette.*

This instrument serves to transfer a definite volume of a fluid from one vessel to another; it must accordingly be of a suitable shape and construction to admit its being freely inserted into the neck of the flask.

We use pipettes of 1, 5, 10, 20, 50, 100, 200 cub. cent. capacity. The proper shape for pipettes up to 20 cub. cent. capacity is represented in Fig. 7; Fig. 8 shows the most practical form for larger-sized pipettes. To fill a pipette with the fluid which it is intended to transfer from one vessel to another, the lower point of the instrument is dipped into the fluid, and suction applied to the upper aperture, either direct with the lips or through a caoutchouc-tube, until the fluid in the pipette stands a little above the required mark; the upper, somewhat narrowed, ground orifice is then closed with the point of the index of the right hand, which to that end had always better be moistened a little, and, holding the pipette in a perfectly vertical direction, the excess of fluid over the quantity required is made to drop out, by lifting the finger a little. When the fluid in the pipette has fallen to the required level, the drops which may happen to adhere to the outside of the pipette are carefully wiped off, and the contents of the tube are then finally transferred to the other vessel. In this process it is found that the fluid does not run out completely, but that a small portion of it remains adhering to the glass in the point of the pipette; after a time, as this becomes increased by other minute particles of fluid trickling down from the upper part of the tube, a drop gathers at the lower orifice, which may be allowed to fall off from its own weight, or may be made to drop off by a slight shake. If, after this, the point of the pipette be laid against a moist portion of the inner side of the vessel, another minute portion of fluid will trickle out, and, lastly, another trifling droplet or so may be got out by blowing into the pipette through the upper orifice. Now, supposing the operator follows no fixed rule in this respect, letting the fluid, for instance, in one operation simply run out, whilst in another operation he lets it drain afterwards, and in a third blows off the last particles of it from the pipette, it is evident that the respective quantities of fluid delivered in the several operations cannot be quite equal. I prefer in all cases the second method, viz., to lay the point of the pipette, whilst draining, finally against a moist portion of the inner sides of the vessel, which I have always found to give the most accurately corresponding measurements.

The correctness of a pipette is tested by filling it up to the mark with distilled water of 60·8° F., letting the water run out, in the manner just stated, into a tared vessel, and weighing; the pipette may be pronounced correct if 100 c. c. of water of 60·8° F. weigh 99·9 grammes.

Testing in like manner the accuracy of the measurements made with a pipette, we find that one and the same pipette will in repeated consecutive weighings of the contents, though filled and emptied each time with the minutest care, show differences up to 0·010 grm. for 10 cub. cent. capacity, up to 0·040 grm. for 50 cub. cent. capacity.

The accuracy of the measurements made with a pipette may be heightened, by giving the instrument the form and construction shown in Fig. 9.

It will be seen from the drawings that these pipettes are emptied only to a certain mark in the lower tube, and that they are provided with a *compression stop-cock*, a contrivance which we shall have occasion to describe in detail in the next section. This contrivance reduces the differences of measurements with one and the same pipette of 50 cub. cent. capacity. to as little as 0·005 grm.

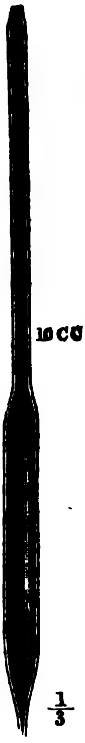

Fig. 7.

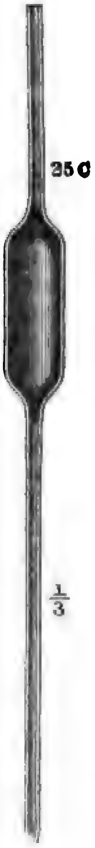

Fig. 8.

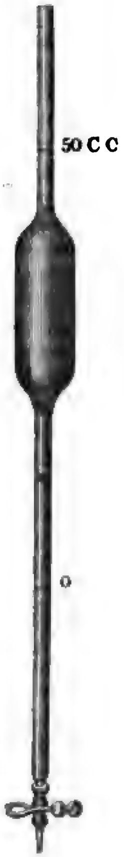

Fig. 9.

Pipettes are used more especially in cases where it is intended to estimate different constituents of a substance in separate portions of the same; for instance, 10 grammes of the substance under examination are dissolved in a flask of 250 cub. cent. capacity, the solution is diluted up to the mark, shaken, and 2, 3, or 4 several portions are then taken out with a pipette of 50 c. c. capacity. Each portion consists of $\frac{1}{5}$ part of the whole, and accordingly contains 2 grammes of the substance.

Cylindrical pipettes, graduated throughout their entire length, may be used also to measure out any given quantities of liquid; however, these instruments can properly be employed only in processes where minute accuracy is not indispensable, as the chances of error in reading off between the divisions in the wider part of the tube are not inconsiderable. For smaller quantities of liquid this inaccuracy may be avoided, by making the pipettes of tubes of uniform width, having a small diameter only, and narrowed at both ends. (Measuring Pipettes of *Fr. Mohr.*)

bb. Measuring vessels which serve to measure out indefinite quantities of fluid.

4. *The Burette.*

Of the various forms and dispositions of this instrument, the following appear to me the most practical and convenient:—

§ 21.

I. *Mohr's Burette,* with caoutchouc Connector and compression Clamp.

For this excellent measuring apparatus, which is represented in Fig. 10, we are indebted to *Fr. Mohr.* It consists, as is shown in the drawing, of a cylindrical tube, tapering towards the lower end, with a slight widening, however, at the extreme point, in order that the caoutchouc connector may take a firmer hold; the narrowest part of the tube measures 25 mm. in length. I only use burettes of two sizes, viz., burettes of 30 cub. cent. capacity, divided into 300 equal parts, each corresponding to $\frac{1}{10}$ of a cub. cent.; and of 50 cub. cent. capacity, divided into 100 equal parts, each corresponding to $\frac{1}{2}$ of a cub. cent.. The former I employ principally in scientific researches, the latter chiefly in technical investigations. The usual length of my 30 c. c. burette is about 50 centimetres; the graduated portion occupies about 43 centimetres. The diameter of the tube is accordingly about 10 mm. in the clear; the upper orifice is widened in form of a funnel, measuring 20 mm. in diameter; the width of the lower orifice is 5 mm. For very delicate processes, the length of the graduated portion may be extended to 50 or 52 centimetres, leaving thus intervals of nearly 2 mm. between the small divisional lines. In my 50 c. c. burettes the graduated portion of the tube is generally 40 centimetres long.

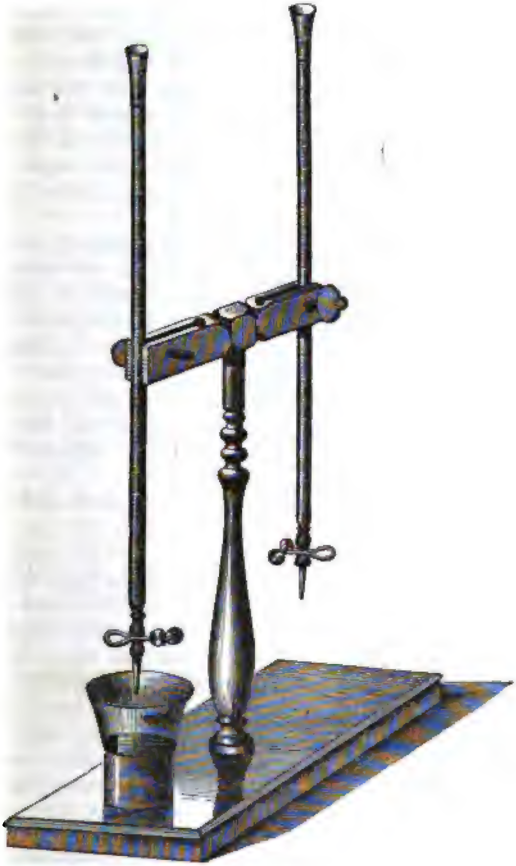

Fig. 10.

To make the instrument ready for use, the narrowed lower end of the tube is warmed a little, and greased with tallow; a caoutchouc tube, about 30 mm. long, and having a diameter of 3 mm. in the clear, is then drawn over it; into the other end of this is inserted a tube of pretty strong glass, about 40 mm. long, and drawn out to a fine point; it is advisable to slightly widen the upper end of this tube also, and to cover it with a thin coat of tallow, in order that the connector may take a firm hold of it; and also to tie linen-thread, or twine, round both ends of the connector, to ensure perfect tightness.

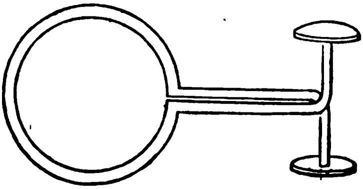

Fig. 11.

The space between the lower orifice of the burette and the upper orifice of the small delivery tube should be about 15 mm. The connector is now pressed together between the ends of the tubes by a brass clamp of the form shown in Fig. 12. (*Mohr* had at first given this clamp the form shown in Fig. 11.)

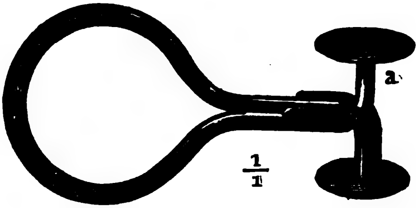

Fig. 12.

A good clamp must pinch so tight that not a particle of fluid can make its way through the connector when compressed by it; it must be so constructed that the analyst may work it with perfect facility and exactness, so as to regulate the outflow of the liquid with the most rigorous accuracy, by bringing a higher or less degree of pressure to bear upon it.

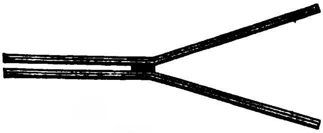

Fig. 13.

*Mohr** has lately devised also very practical clamps made of glass (or horn) and caoutchouc, which I can highly recommend.

Figs. 13 and 14 show the construction of these clamps; they are so simple that anybody may easily make them according to *Mohr's* instructions, which I will give here in his own words:—

"Bend two pieces of flat thermometer tubing from 80 to 90 mm. long, in a very obtuse angle, place between them, in the middle, a piece of cork, about 1½ or 2 mm. thick, and put a caoutchouc ring, cut off from a somewhat wide india-rubber tube, over the part enclosing the cork.

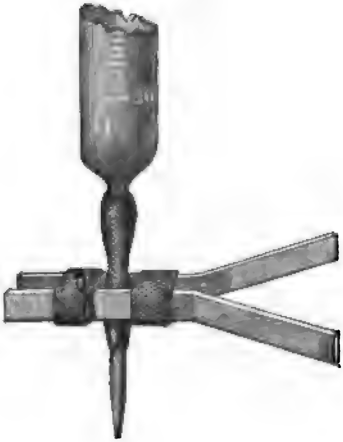

Fig. 14.

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* *Mohr's* "Lehrbuch der Titrirmethode," addenda, p. 344.

Put the little caoutchouc tube of the burette between the two glass tubes, press the points together, and push another india-rubber ring over the tubes. These two rings serve to keep the connector of the burette tightly compressed. By pressing on the divergent ends of the glass rods, the elastic bands are stretched asunder, and the connector being thus partly relieved from the compression exerted by them, allows the liquid to drop through the delivery tube; when the pressure on the ends of the tube ceases, the elastic bands, recovering their original tightness, close the connector again."

For fixing *Mohr's* burettes, I use the holder represented in Fig. 10; this instrument, whilst securely confining the tube, permits its being moved up and down with perfect freedom, and also its being taken out and removed, without interfering with the compression clamp. The position of the burette must be strictly perpendicular, to ensure which, care must be taken to have the grooves of the cork lining, which are intended to receive the tube, perfectly vertical, with the lower board of the stand in a horizontal position. A similar holder, with brass screw-clamp, is represented in Fig. 15.

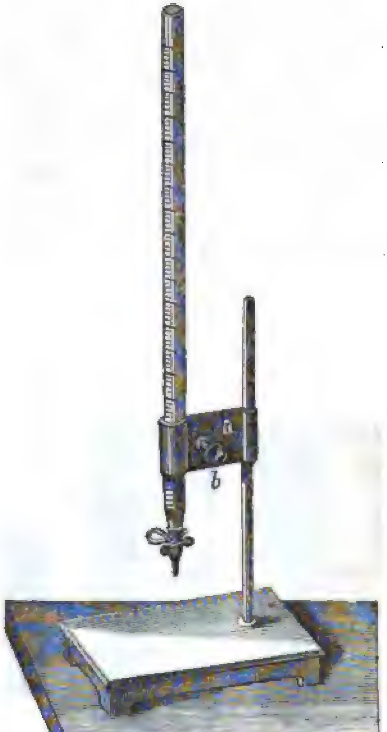

Fig. 15.

To charge the burette for a volumetrical operation, the point of the instrument is immersed in the liquid, the connector opened, by working the clamp, and a little liquid, sufficient at least to reach into the burette tube, sucked up by applying the mouth to the upper end; the connector is then compressed again, and the liquid poured into the burette through the upper orifice until it reaches up to a little above the upper line-mark. The burette having, if required, been duly adjusted in the proper vertical position, the liquid is allowed to drop out until the exact level of the upper line-mark is reached. The instrument is now ready for use. When as much liquid has flown out as is required to attain the desired object, the analyst, before proceeding to read off the volume used, has to wait a few minutes, to give the particles of fluid adhering to the sides of the emptied portion of the tube proper time to run down. This is an indispensable part of the operation in accurate measurements, since, if neglected, an experiment in which the standard liquid in the burette is added slowly to the fluid under examination (in which, accordingly, the minute particles of fluid adhering to the glass have proper time afforded them during the operation itself to run down), will, of course, give slightly different results from those arrived at in another experiment, where the larger portion of the standard fluid is applied rapidly, and the last few drops alone are added slowly.

The *way* in which the *reading-off* is effected, is a matter of great importance in volumetrical analyses; the first requisite is to bring the eye to a level with the surface of the fluid, and also to adopt a fixed and unalterable standard of what is to be considered the surface.

If you hold a burette, partly filled with water, between the eye and a strongly illumined wall, the surface of the fluid presents the appearance shown in Fig. 16; if you hold close behind the tube a sheet of white paper, with a strong light falling on it, the surface of the fluid presents the appearance shown in Fig. 17.

In the one as well as in the other case, you have to read off at the lower border of the dark zone, this being the most distinctly marked line. It may be made more distinct still by the following simple contrivance devised by *Fr. Mohr:* paste on a sheet of very white cardboard a broad strip of black paper, and, when reading-off, hold this close behind the burette, in a position to place the border line between white and black from 2 to 3 mm. below the lower border of the dark zone, as shown in Fig. 18.

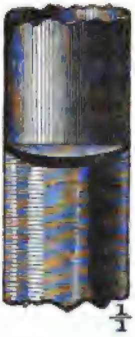
Fig. 16.

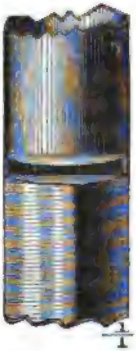
Fig. 17.

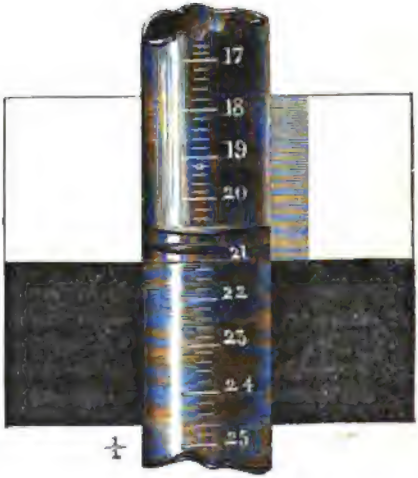

Fig. 18.

Great care must be taken to hold the paper invariably in the same position, since, if it be held lower down, the lower border of the black zone will move higher up.

The correctness of the graduation of a burette is tested in the most simple way, as follows: fill the instrument up to the highest division with water of 60·8° F., then let 10 cub. cent. of the liquid flow out into an accurately weighed flask, and determine the weight of these 10 cub. cent. in the usual way; then let another quantity of 10 cub. cent. flow out, and weigh again, and repeat the operation until the contents of the burette are exhausted. If the instrument is correctly graduated, every 10 cub. cent. of water of 60·8° F. must weigh 9·990 grammes. Differences up to 0·010 grm. may be disregarded, since even with the greatest care bestowed on the process of reading-off, deviations to that extent will occur in repeated measurements of the uppermost 10 cub. cent. of one and the same burette.

Mohr's burette is unquestionably the best and most convenient and practical instrument of the kind, and ought to be employed in the measurement of all liquids which are not injuriously affected by contact with caoutchouc. Of the standard solutions used at present in volumetrical analysis, that of permanganate of potassa alone cannot bear contact with caoutchouc.

§ 22.

II. *Gay-Lussac's Burette.*

Fig. 19 represents what I consider the most practical form of this instrument.

I make use of two sizes, one of 50 cub. cent. capacity, divided into half-cubic centimetres, the other of 30 cub. cent. capacity, divided into 300 equal parts, each corresponding to the $\frac{1}{10}$ of a cub. cent. The former is about 33 centimetres long; the graduated portion occupies about 25 centimetres; the internal diameter of the wide tube measures 15 mm.; that of the narrow tube 4mm., which in the upper bent end gradually decreases to 2 mm. The graduated portion of the smaller burette (30 c. c., divided into 300 parts) is about 28 centimetres long, and has accordingly an internal diameter of about 11 mm.

When operating with a burette of this construction, I hold the instrument with the left hand, letting the bottom part lean a little against the chest. This way of handling the instrument gives the operator the most perfect control over it, and enables him to regulate at will the outflow of the liquid; the operation may be facilitated also by giving the burette, from time to time, a slight turn in the direction of its longitudinal axis, thereby placing the curve of the spout alternately in a more vertical, alternately in a more horizontal, position. As a general rule, I never let the liquid run back in the narrow tube, in the course of an experiment, since the air-bubble enclosed between the fluid in the burette and the drop adhering to the mouth of the spout, makes it generally a task of some difficulty to renew the outflow of the liquid.

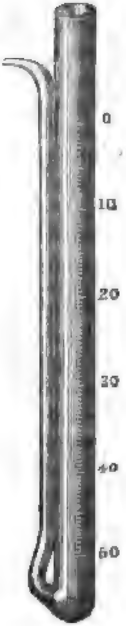

Fig. 19.

The stand which I make use of to rest my burettes in, consists of a disk of solid wood, from 5 to 6 centimetres high, and from 10 to 12 centimetres in diameter, with holes made with the auger or the chisel, of proper size to receive the bottom part of the burette. This arrangement seems to me more convenient than the common method of cementing the burette in a wooden foot.

To overcome the difficulty of renewing the outflow of the liquid, which is always experienced when, during the temporary cessation of the process, air has been enclosed between the liquid in the burette and the drop adhering to the mouth of the spout, *Mohr* suggests the use of a perforated cork, bearing a short glass tube bent at a right angle. The cork being inserted into the mouth of the wide tube, a piece of caoutchouc is drawn over the short glass tube; by blowing into this with greater or less force, the outflow of the liquid from the spout of the burette may be regulated at pleasure.

The reading off of the height of the liquid is effected in the same way as explained in § 21. I prefer, however, placing the burette firmly against a perpendicular partition, either a strongly illumined door, or the pane of a window, to ensure the vertical position of the instrument. It is only when operating with more highly concentrated, and accordingly opaque solutions of permanganate of potassa, that the method of reading off requires some slight modification, since, in that case, the upper border of the dark zone is held to be the limit of the liquid; and the best way, accordingly, is to place the burette against a white background, and read off by reflected light.

The correctness of the graduation of *Gay-Lussac's* burettes is tested in the same way as that of *Mohr's* burettes.

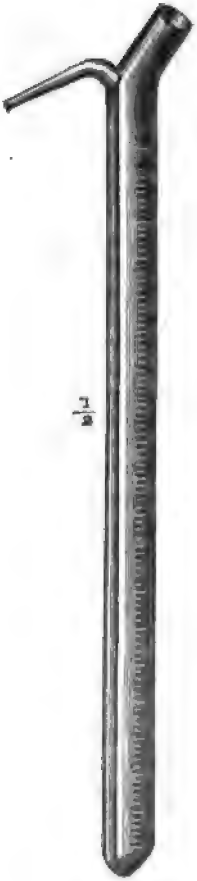

Fig. 20.

§ 23.

III. *Geissler's Burette.*

In this instrument, which is represented in Fig. 20, the narrow tube is placed inside the wide tube instead of outside, as in *Gay-Lussac's* burette. The spout projecting beyond the wide tube is thick in the glass; whilst the part inside, which is of uniform width throughout its entire length, is made of very thin glass.

This is a very convenient and practical instrument, and less liable to fracture than *Gay-Lussac's* burette. I like to work with it.

For the method of reading-off and testing the correctness of the instrument, I refer to §§ 21 and 22.

II. Preliminary Operations.—Preparation of Substances for the Processes of Quantitative Analysis.

§ 24.

1. The Selection of the Sample.

Before the analyst proceeds to make the quantitative analysis of a body, he cannot too carefully consider whether the desired result is fully attained if he simply knows the respective quantity of every individual constituent of that body. This primary point is but too frequently disregarded, and thus false impressions are made, and wrong notions created, even by the most careful analysis. This remark applies both to scientific, and to technical investigations.

Therefore, if you have to determine the composition and constitution of a mineral, take the greatest possible care to remove, in the first place, every particle of gangue and disseminated impurities; then wrap the ore up in a sheet of thick paper, and crush it to pieces on a steel anvil; select and pick out with a pair of small pincers the cleanest pieces. Crystalline substances, prepared artificially, ought to be purified by recrystallization; precipitates by thorough washing, &c. &c.

In technical investigations—when called upon, for instance, to determine the amount of peroxide present in a manganese ore, or the amount of iron present in an iron ore, &c.—the first point for consideration ought to be whether the samples selected correspond as much as possible to the average quality of the ore. What would it serve, indeed, to the purchaser of a manganese mine to know the amount of peroxide present in a select, and probably particularly rich, sample?

These few observations will suffice to show that no universally applicable and valid rules to guide the analyst in the selection of the sample can be laid down; he must in every individual case, on the one hand, examine the substance carefully, and more particularly also under the microscope, or through a lens; and, on the other hand, keep clearly in view the *object* of the investigation, and then take his measures accordingly.

§ 25.

2. MECHANICAL DIVISION, OR DISINTEGRATION.

In order to prepare a substance for analysis, *i. e.*, to render it accessible to the action of solvents or fluxes, it is generally indispensable, in the first place, to divide it into minute parts, since this will create abundant points of contact for the solvent, and will counteract, and, as far as practicable, remove the adverse influence of the power of cohesion, thus fulfilling the principal conditions necessary to effect a complete and speedy solution.

The means employed to attain this object, vary according to the nature of the different bodies we have to operate upon. In many cases, simple crushing or pounding is sufficient; in other cases it is necessary to reduce the powder to the very highest degree of fineness, by sifting or by elutriation.

The operations of pounding and levigating are conducted in mortars or on levigating slabs; the first and most indispensable condition is, that the material of the mortar, dish, or slab be considerably harder than the substance to be pulverized, so as to prevent, as far as practicable, the latter from being contaminated with any particles of the former. Thus, for pounding salts and other substances possessing no very considerable degree of hardness, porcelain mortars may be used, whilst the pounding of harder substances (of most minerals, for instance), requires vessels of agate, chalcedony, or flint. In such cases, the larger pieces are first reduced to a coarse powder; this is best effected by wrapping them up in several sheets of paper, and striking them with a hammer upon a steel or iron plate; the coarse powder thus obtained is then pulverized, in small portions at a time, in an agate mortar, until it is completely reduced to the state of an impalpable powder. If we have but a small portion of a mineral to operate upon, and indeed in all cases where we are desirous of avoiding loss, it is advisable to use a steel mortar for the preparatory reduction of the mineral to coarse powder. Fig. 21 represents a mortar adapted for this purpose.

a b and *c d* represent the two component parts of the mortar; these may be readily taken asunder. The substance to be crushed (having, if practicable, first been broken into small pieces), is placed in the cylindrical chamber *e f*; the steel cylinder *f g*, which fits somewhat loosely into the chamber, serves as pestle. The mortar is placed upon a solid support, and perpendicular blows are repeatedly struck upon the pestle until the object in view is attained.

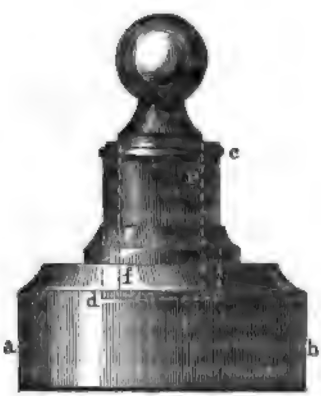

Fig. 21.

Minerals which are very difficult to pulverize should be ignited, and, when red hot, suddenly plunged into cold water, and subsequently again ignited, if necessary. This process is of course applicable only to minerals which lose no essential constituent at a red heat, and are perfectly insoluble in water.

In the purchase of agate mortars, especial care ought to be taken that they have no palpable fissures or indentations; very slight fissures, however, do not render the mortar useless, although they impair its durability.

Minerals insoluble in acids, and which consequently require fluxing, must be divided as finely as possible, otherwise we cannot calculate upon complete decomposition. This object may be obtained either by triturating the pounded mineral with water, or by elutriation, or by sifting; the two former processes, however, can be resorted to only in the case of substances which are not attacked by water. It is quite clear that analysts must in future be much more cautious in this point than has hitherto been the case, since we know now that many substances which are usually held to be insoluble in water are, when in a state of minute division, strongly affected by that solvent; thus, for instance, water, acting upon finely pulverized glass, is found to rapidly dissolve from 2 to 3 per cent. of the powder even in the cold. (*Pelouze*, "Compt. Rend." t. xliii., pp. 117-123.)

Trituration with water (*levigation*). Add a little water to the pounded mineral in the mortar, and triturate the paste until all crepitation ceases, or, which is a more expeditious process, transfer the mineral paste from the mortar to an agate, flint, or porphyry slab, and triturate it thereon with a muller until it is perfectly smooth. Rinse the paste off, with the washing bottle, into a smooth porcelain basin of hemispheric form, evaporate the water on the water-bath, and mix the residue most carefully with the pestle. (The paste may be dried also in the agate mortar, but at a very gentle heat, since otherwise the mortar might crack.)

To perform the process of *elutriation*, the pasty mass, having first been very finely triturated with water, is washed off into a beaker, and stirred with distilled water; the mixture is then allowed to stand a minute or so, after which the supernatant turbid fluid is poured off into another beaker. The sediment, which contains the coarser parts, is then again subjected to the process of trituration and elutriation, &c.,

and the same operation repeated until the end in view is attained. The turbid fluid collected from the successive decantations is allowed to stand at rest until the minute particles of the substance held in suspension have subsided, which generally takes many hours. The clear supernatant fluid is then finally decanted, and the powder dried in the beaker.

The process of *sifting*, or *dusting*, is conducted as follows: a piece of fine, well-washed, and thoroughly dry linen is placed over the mouth of a powder glass, about 10 centimetres high, and pressed down a little into the mouth, so as to form a kind of bag; a portion of the finely triturated substance is put into the bag, and a piece of soft leather stretched tightly over the orifice, by way of cover. By drumming with the finger on the leather cover, a shaking motion is imparted to the bag, which makes the finer particles of the powder gradually pass through the linen. The portion remaining in the bag is subjected again to trituration in an agate mortar, and, together with a fresh portion of the powder, sifted again; and the same process is continued until the entire mass has passed through the bag into the glass, in form of a most intimately mixed, dusty powder.

When operating on compound and mixed minerals, it would be a grave error indeed to use for analysis the powder resulting from the first process of elutriation or sifting, since this will contain the more readily pulverizable parts in a greater proportion to the more resisting parts, than is the case with the original substance.

Great care must, therefore, also be taken to avoid a loss of substance in the processes of elutriation and sifting, as this loss is likely to be distributed unequally among the several component parts.

In cases where it is intended to ascertain the average composition of a mixed substance, of an iron ore for instance, a large average sample is selected, and reduced to a coarse powder; the latter is thoroughly intermixed, and a portion of it then brought to the requisite degree of fineness. The most convenient and best-adapted instrument for the crushing and coarse pounding of large samples of ore, is a steel anvil and hammer. The anvil in my own laboratory consists of a wood pillar, 85 centimetres high and 26 centimetres in diameter, into which a steel plate, 3 centimetres thick and 20 centimetres in diameter, is let to the depth of one-half of its thickness. A brass ring, 5 centimetres high, is put round the upper projecting part of the steel plate. The hammer, which is well steeled, has a striking surface of 5 centimetres diameter. An anvil and hammer of this kind afford, among others, this advantage, that their steel surfaces admit most readily of cleaning.

§ 26.

3. Desiccation, or Drying.

Substances which it is intended to analyse must be submitted to the requisite operations and processes in a clearly and distinctly characterized and definite state or form.

In our introductory remarks we have laid it down as an indispensable condition of quantitative analysis, that the *kind* and *nature of the constituents* of the compounds under examination must be *exactly* and *accurately* known before we can proceed to their quantitative estimation. Now, the essential constituents of a substance are usually accompanied by an accidental admixture, viz., a greater or less amount of water, inclosed either within its lamellæ, or adhering to it from the mode of its preparation, or absorbed by it from the atmosphere. It is perfectly obvious that to estimate correctly the quantity of a substance, we must, in the first place, remove the water which it may happen to hold in admixture. *Most solid bodies,* therefore, *require to be dried before they can be quantitatively analysed.*

The operation of drying is of the very highest importance for the correctness of the results; indeed it may safely be averred that many of the differences observed in analytical researches proceed entirely from the fact that substances are analysed in different states of moisture.

It must be borne in mind, of course, that many substances contain water among their *essential* constituents (constitutional, or basic, water, and water of crystallization). With this water we must not interfere; the operation of drying, which we have here in view, is intended only to remove the water accidentally admixed, or mechanically adhering to the substance, and which we will term here "*moisture,*" the better to distinguish it from the water essentially inherent in a substance. Accordingly, in the drying of substances for quantitative analysis, our only object is to remove all *moisture* from them, without interfering, in the slightest degree, with their *constitutional* water, or any other *essential* constituent. To accomplish this object, it is absolutely requisite that we should know the properties which the substance under examination manifests in the *dry* state, and whether it loses water or other constituents at a red heat, or at 212° F., or in dried air, or even simply in contact with the atmosphere. These data will serve to guide us in the selection of the process of desiccation best suited to the substance under examination.*

The following classification may accordingly be adopted:—

a. Substances which yield water even in simple contact with the atmosphere; such as sulphate of soda, crystallized carbonate of soda, &c. Substances of this kind turn dull and opaque when exposed to the air, and finally crumble wholly or partially to a white powder. They are more difficult to dry than many other bodies. The process best adapted for the purpose, is to press the pulverized salts with some degree of force between thick layers of fine blotting-paper, until the last sheets remain *absolutely dry.*

It is generally advisable to subject the pulverized salts, in the course of this operation, once more to the process of trituration.

b. Substances which do not yield water to the atmosphere (*unless perfectly dry*), *but effloresce in artificially dried air;* such as sulphate of magnesia, tartrate of potassa and soda (Rochelle salt), &c. Salts of this kind are reduced to a fine powder, which, if it be very moist, is pressed between sheets of blotting-paper, as in *a;* after this operation, it must be allowed to remain for some time spread in a thin layer upon a sheet of blotting-paper, effectually protected against dust, and shielded from the direct rays of the sun.

§ 27.

c. Substances which undergo no alteration in dried air, but lose water

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* The dried substance should always at once be transferred to a well-closed vessel; glass tubes, sealed at one end, and of sufficiently thick glass to bear the firm insertion of tight-fitting smooth corks, are usually employed for this purpose. It is advisable to put tinfoil under the cork.

at 212° F.; tartrate of lime, for instance. These are finely pulverized; the powder is put in a thin layer into a watch-glass or shallow dish, and the latter placed inside a bell-glass, in which the air is kept dry by means of sulphuric acid. This process is usually conducted in one of the apparatus illustrated by Figs. 22 and 23, which are technically termed *desiccators*, and subserve still another purpose besides that of drying, viz., to allow hot crucibles, dishes, &c., to cool in dry air.

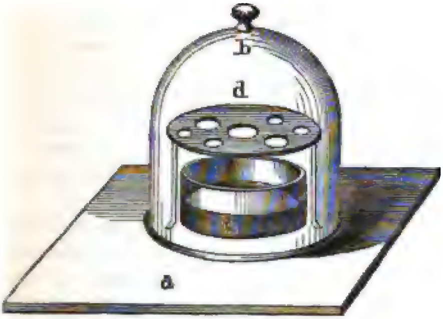

Fig. 22.

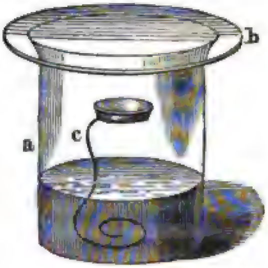

Fig. 23.

In Fig. 22, *a* represents a glass plate (ground glass plates answer the purpose best), *b* a bell jar, with ground rim, which is greased with tallow; *c* is a glass basin with sulphuric acid; *d* a round iron plate, supported on three feet, with circular holes of various sizes, for the reception of the watch-glasses containing the substances to be dried, or of crucibles in course of cooling, &c.

In Fig. 23, *a* represents a beaker with ground rim, and filled to *one-fourth* or *one-third* with concentrated sulphuric acid; *b* is a ground-glass plate, the rim of which is smeared with tallow; *c* is a bent wire of lead, which serves to support the watch-glass containing the substance to be dried.

Fig. 24 represents a portable exsiccator, used more particularly to receive crucibles in course of cooling, and carry them to the balance. The instrument consists of a box made of strong glass; the lid must be ground to shut air-tight; the place on which it joins is greased with tallow. The outer diameter of my boxes is 105 mm.; the sides are 6 mm. thick. The aperture has a diameter of 80 mm.; the box up to the groove is 65 mm. high; the lid has the same height; the rim above the groove is 15 mm. high, and ground to a slightly conical shape. A brass ring, with grooved rim fitting close under the glass, fits exactly into the aperture; the upper border of the ring must not project above the glass. The ring bears a triangle of iron, or, better, platinum wire, intended for the reception of crucibles, &c.

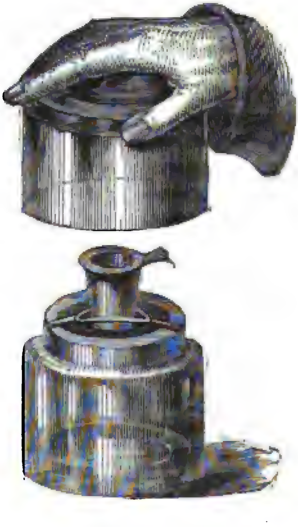

Fig. 24.

Fig. 25 represents the desiccator constructed by *A. Schrötter*, upon the principle of affording free egress to the air, which expands as soon as hot crucibles are placed inside the apparatus; the expanding air escapes, in the first place, through the little tube *a*, then through the two lateral apertures in the lower part of *b*; the air-bubbles lastly, which ascend through the sulphuric acid in *c*, make their escape from the bulb *d*, which is filled with chloride of calcium. When the apparatus is cooling, perfectly dry air re-enters by the same way. The operation may be considered at an end when no more air-bubbles ascend through the sulphuric acid. The little tube *e* serves to catch the sulphuric acid that might be carried down through *a*; this tube must not close the lower orifice of the bell-jar air-tight, and the cork holding it must be channelled: *f* serves as stand for the bell-glass. This desiccator affords the advantage that the substances placed in it are cooled in dry air of the common pressure, and have accordingly, when removed from the apparatus, no tendency to attract moist air, which cannot be said of substances cooled in air slightly rarefied by heat. The body which it is intended to dry is kept exposed to the action of the dry air in the glass, until it shows no further diminution of weight. Substances upon which the oxygen of the air exercises a modifying influence are dried in a

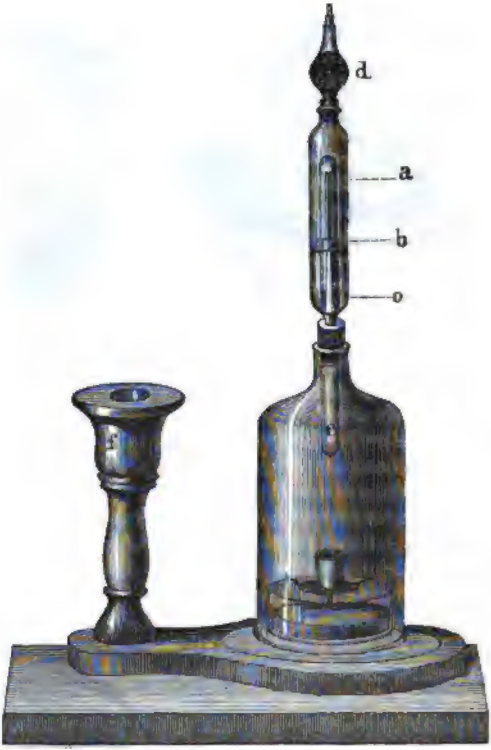

Fig. 25.

similar manner, under the exhausted receiver of an air-pump. Substances which, though losing no water in dry air, yet give off ammonia, are dried over calcined lime, mixed with some chloride of ammonium in powder, and consequently in an anhydrous ammoniacal atmosphere.

§ 28.

d. Substances which at 212° F. *completely lose their moisture, without suffering any other alteration*, such as bitartrate of potassa, sugar, &c. These are dried in the water-bath; in the case of slow-drying substances, or where it is wished to expedite the operation, with the aid of a current of dry air.

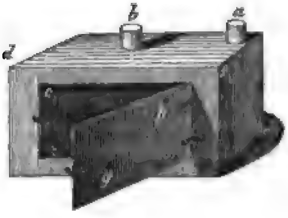

Fig. 26.

Fig. 26 represents the water-bath most commonly used. It is made either of sheet tin, or, better, of sheet copper, and is soldered with brass, to adapt it for use also as an oil-bath. The engraving renders a detailed explanation unnecessary. The inner chamber, *c*, is surrounded on five sides by the outer case or jacket, *d e*, without communicating with it. The object of the apertures *g* and *h* is to effect change of air, which purpose they answer sufficiently well. When it is intended to use the apparatus, the outer case is filled to about one-half with rain-water, and the aperture *a* is closed with a perforated cork, into which a glass tube is fitted; the aperture *b* is entirely closed. If the apparatus is intended to be heated over charcoal, it should have a length of about 20 centimetres from *d* to *f*; but if over a gas-, spirit- or oil-lamp, it should be only about 13 centimetres long. In the former case, the inner chamber is 17 centimetres deep, 14 centimetres broad, and 10 centimetres high; in the latter case, it is 10 centimetres deep, 9 centimetres broad, and 6 centimetres high. The temperature in the inner chamber never quite reaches 212° F.; to bring it up to 212° F., *F. Rochleder* has lately suggested to close *b* with a double-limbed tube, the outer longer limb of which dips into a cylinder filled with water; *a* is in that case closed with a perforated cork bearing a sufficiently tall funnel tube, which fits air-tight in the cork. The lower end of this tube reaches down to one inch from the bottom. In large analytical laboratories water is usually kept boiling all day long, for the production of distilled water. The boilers used in my own laboratory have the shape of somewhat oblong square boxes, about 120 centimetres long, 60 centimetres broad, and 24 centimetres high; the front side of the boiler has soldered into it, one above the other, two rows of drying-chambers, or closets, of the kind shown in Fig. 26. This gives a sufficient number of drying-chambers to enable me to afford the special use of one of them to almost every student in the laboratory. Most of these little apparatus are from 11 to 12 centimetres long and broad, and 8 centimetres high; some of them, however, are 16 centimetres long and broad, to fit them to receive also larger-sized dishes. The substances to be dried are usually put on double watch-glasses, laid one within the other, which are placed in the inner chamber; the apparatus is then closed. In the subsequent process of weighing, the upper glass, which contains the substance, is covered with the lower one. The glasses must be quite cold before they are placed on the scale. In cases where we have to deal with hygroscopic substances, the re-absorption of water upon cooling is prevented by the selection of close-fitting glasses, which are held tight together by a clasp (Fig. 27), and allowed to cool with their contents under a bell-glass over sulphuric acid (see Fig. 22). These latter instructions apply equally to the process of drying conducted in other apparatus.

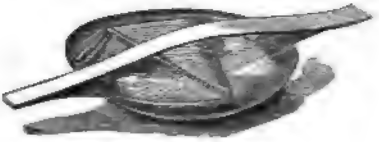

Fig. 27.

The clasps used for keeping the watch-glasses pressed together—and which in all cases where it is intended to ascertain the loss of weight which a substance suffers on desiccation, are to be looked upon as part and parcel of the glasses, and must accordingly be weighed with them—are constructed of two strips of thin brass plate, about ten centimetres long, and one centimetre wide, which are laid the one over the other, and soldered together at the ends, to the extent of 5 to 6 millimetres.

The following apparatus serve for drying substances in a current of air.

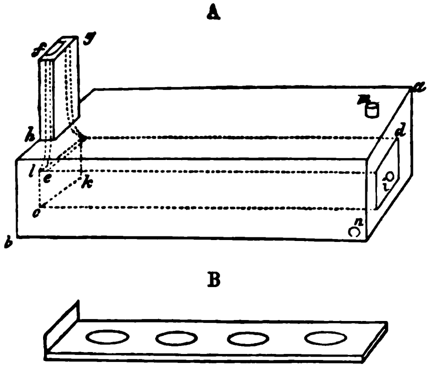

Fig. 28.

In Fig. 28 (A) the current is caused simply by heating the air, which renders this apparatus very convenient for use.

a b is a case of sheet copper, or sheet tin, into which the canal *c d* is soldered; the latter communicates with the chimney *e f*; this is surrounded on three sides by the cover *g h*, which again communicates with *a b*. The cover has no opening at the top. At *i* is a round aperture leading into the canal, and which may be closed with a cork; *l k* is provided with a well-fitting sliding lid running in grooves.

The operation is commenced by filling the case *a b* to one half with water, through the aperture *m*—the aperture *n*, which serves to let off the water, being closed with a cork—and heat is then applied to raise the temperature of the water to the boiling-point. The watch-glasses with the substances to be dried are placed into the hollows of the sliding shelf, B, and the latter is introduced into the canal *c d* at *l k*, which is then closed by the sliding lid.

The air in the canal, becoming heated by the surrounding steam, ascends, and the cold atmospheric air flowing in through the aperture *i* and passing over the drying substances, carries away with it the evaporating moisture. There is a slight disadvantage attending this mode of proceeding, viz., the cold air which passes through *i* keeps the drying substances always a little below 212° F.; this may be easily remedied, however, by conducting the air, in the first place, through a tube running along under the bottom of the canal down to *l k*, and returning thence to the other extremity, where it is finally fitted into *i*; this tube must be soldered in its whole length to the outer lower surface of the canal. The air conveyed through this tube is thus heated to 212° F., before coming into contact with the drying substance. This tube has been omitted from the engraving, to avoid confusion.

To render the apparatus still more useful, round holes of different sizes may be cut in the top of the case; these holes, for which proper covers must be provided, serve for the reception of small evaporating dishes. The aperture *m* may, in that case, be omitted, as the water may be poured in through one of the holes. The apparatus is, according to the requirements of the case, made from 20 to 30 centimetres long, with a depth and height of about 10 centimetres. The canal should be 5 centimetres wide, and 2·5 centimetres high.

If it be desirable to create a stronger draught of air than that produced by the little chimney, air which has previously been transmitted through sulphuric acid, or through a chloride of calcium tube, may be blown into *i* by means of a gasometer, or an india-rubber balloon, or some other contrivance.

If a higher temperature than that of boiling water be required, the outer (copper) case is filled with oil, and the temperature determined by a thermometer, fixed into *m* by a cork.

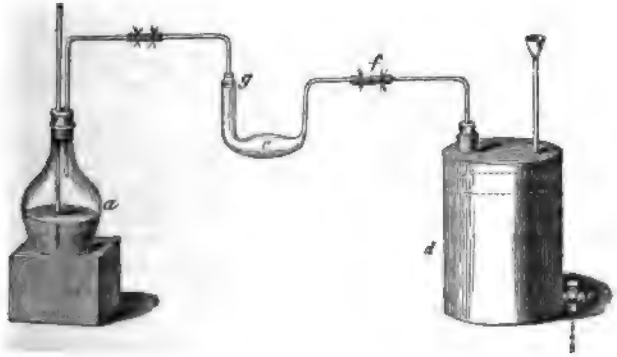

Fig. 29.

In the apparatus represented in Fig 29, the current of air is produced by an aspirator.

a represents a flask filled to one-third with concentrated sulphuric acid; *c* a glass vessel, commonly called a Liebig's drying-tube; and *d* a tin vessel, provided with a stop-cock at *e*, and arranged in other respects as the engraving shows.

Fig. 30 represents a small tin vessel, containing water and covered with a lid; two apertures, *a* and *b*, are cut into the border of the latter, to receive the ascending limbs of *c*.

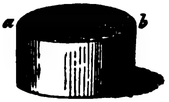

Fig. 30.

The substance intended for drying is accurately weighed, and placed in the tube *c*, the exact weight of which has also been previously ascertained; *c* is then suspended in the vessel represented in Fig. 30, and the water contained in the latter is heated to boiling, by means of a spirit- or gas-lamp; the tin vessel *d* is then filled with water, and *c* connected with the flask *a* by the perforated cork *g*, and with *d* by means of a caoutchouc tube *f*. If the stop-cock *e* be now opened so as to cause the water to flow from *d*, the air will pass through the tube *b* into *a*; its moisture will be retained by the sulphuric acid, and the dry air will then pass over the heated substance in *c*. After the operation has been continued for some time, it is interrupted for the purpose of weighing the tube *c* and its contents, and then resumed again, and continued until the weight of *c* (and its contents) remains stationary. The current of cold air, exercising its constant cooling action upon the drying substance, the latter never really reaches a temperature of 212° F. It is, therefore, sometimes advisable to substitute for the water in Fig. 30 a saturated solution of common salt.

With this substitution, the apparatus represented in Figs. 29 and 30 will be found to effect its purpose expeditiously. It is not adapted, however, for drying such substances as have a tendency to fuse or agglutinate at 212° F.

§ 29.

e. Substances which do not completely lose their moisture at 212° F., *or the perfect desiccation of which requires a long-protracted exposure to that temperature; but which are decomposed by a red heat.*

The desiccation of such substances is effected in the air-bath or oil-bath, or the drying-disk is resorted to, the temperature being raised to 230°—248° F., and still higher, and, according to circumstances, with or without application of a current of air; in some cases in rarefied air, in others in dilute carbonic acid.

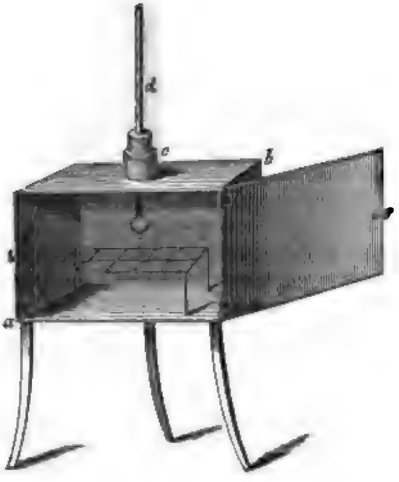

Fig. 31.

Figs. 31 and 32 represent two air-baths of the simplest construction; the former (Fig. 31) adapted for the simultaneous drying of several substances, the latter more particularly suited for the desiccation of a single substance.

In Fig. 31, *a b* is a case of strong sheet copper, soldered with brass, of a width and depth of 15 to 20 centimetres, and corresponding height. The aperture *c* is intended to receive a perforated cork, into which is fixed a thermometer, *d*, which reaches into the interior of the case; *e* is a wire stand, on which are placed the watch-glasses with the substances to be dried. The case is heated by means of a gas-, spirit-, or oil-lamp. When the temperature has once reached the intended point, it is easy to maintain it pretty constant, by regulating the flame.*

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* With a gas-lamp, *Kemp's* regulator improved by *Bunsen*, may advantageously be used to obtain constant temperatures. This regulator may be procured at Mr. Griffin's, Bunhill-row, London.

In order to lessen as much as possible the chance of cooling from without, it is advisable to put over the whole apparatus a pasteboard hood with a moveable front.

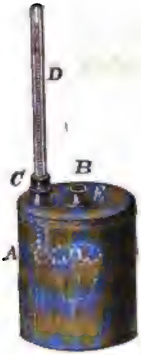

Fig. 32.

In Fig. 32, *a* is a box of strong sheet copper, about 11 centimetres high, and 9 centimetres in diameter. The box is closed with the loose-fitting cover *b*, which is provided with a narrow rim, and has two apertures, *c* and *e*. *c* is intended to receive the thermometer *d*, which is fitted into it by a perforated cork. *e* affords an exit to the aqueous vapors, and is, according to circumstances, either left open, or loosely closed. In the interior of the box, about half way up, are fixed three pins, supporting a triangle of moderately stout wire, upon which the crucible with the substance is placed uncovered. The ball of the thermometer approaches the crucible as close as possible, but without touching the triangle. The heating is effected by means of a gas- or spirit-lamp. When the apparatus has cooled sufficiently to allow its being laid hold of without inconvenience, the lid is removed, the crucible, which is still warm, taken out, covered, and allowed to cool in a desiccator; and weighed when cold.

The air-bath represented in Fig. 33 serves for the desiccation of substances in a bulb-tube, with simultaneous application of a current of dry air.

The apparatus consists of a hollow box, made of sheet iron, of the following dimensions:—$ab = 20$, $ac = 13$, $ad = 12$, $ef = 11$, $eg = 6$ centimetres. These dimensions answer the purpose perfectly well. The apertures of both sides, provided with short projecting rim, have a diameter of 16 mm. The thermometer is pushed down sufficiently far to place it in the same line with the bulb of the tube of the box, the two bulbs being thus brought into lateral contact with each other. To this end, the aperture *h* must not be placed in the central line, but 1 centimetre in the rear of it. It is easy to give the chamber of this apparatus a temperature of from 392° to 500° F. To pro-

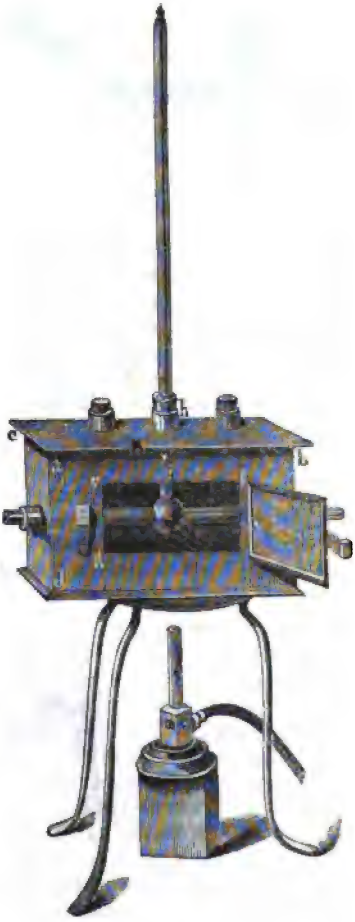

Fig. 33.

duce the current of dry air, one of the projecting ends of the bulb-tube is connected with an aspirator, as in Fig. 29, the other with a chloride of calcium tube; the water of the aspirator is allowed to drop out, somewhat rapidly at first, more slowly after. If it is intended to weigh the tube with the dried substance, it is allowed to cool, with a current of dry air still continuing to pass through.

In the air-bath (illustrated by Fig. 34) the drying is promoted by alternate exhaustion and re-admission of air.

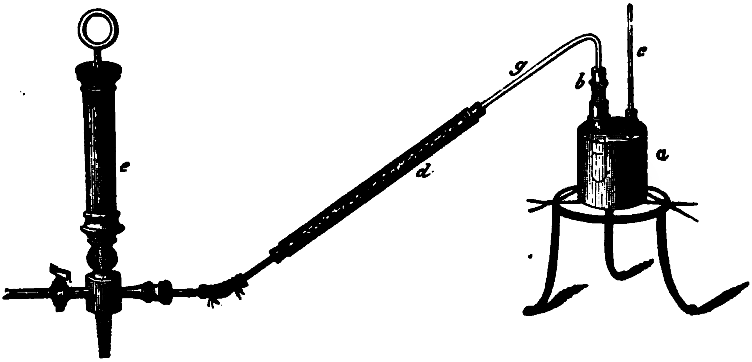

Fig. 34.

a represents a vessel of strong sheet copper, soldered with brass, and provided with two apertures at the top; *b* is a small glass tube, containing the substance intended for desiccation; *c* a thermometer; *d* a tube with chloride of calcium; *e* an exhausting syringe.

The operation is commenced by heating *a* to the desired degree; *b* and *d* are then exhausted by working the syringe. After the lapse of a few minutes, fresh air is re-admitted through the stop-cock *f*, which, passing over the chloride of calcium in *d*, is completely freed from moisture. The same process of alternate exhaustion and re-admission of air is repeated until the interior of the tube *g* ceases to exhibit even the faintest trace of moisture, when cooled by the application of cotton saturated with ether.

§ 30.

The copper apparatus represented in Fig. 26, is employed also as an oil-bath; when used for that purpose, the outer case is filled to two-thirds with refined rape-oil. To note the temperature, a thermometer is inserted, by means of a perforated cork, in the aperture *a*; with the bulb reaching nearly to the bottom, but, at all events, entirely immersed in the oil. As the oil, when heated, emits a most disagreeable smell, I often use paraffine instead, which may now be had very cheap. The air-bath represented in Fig. 34, will also serve the purpose of an oil-bath. If it is intended to weigh the substance after drying in a tube, a shorter tube is selected for the purpose, which readily admits of insertion into the tube standing in the oil.

Many organic substances, when dried at a higher temperature, suffer alteration by the action of the atmospheric oxygen.* In the desiccation of such substances, oxygen must accordingly be excluded.

Fig. 35 represents the apparatus devised for that purpose by *Rochleder*.

The part H is screwed on at *a*, to the air-pump; *b* is connected, by means of an india-rubber tube, with a caoutchouc-bag (or a bladder), filled with carbonic acid. B is an oil-bath; the temperature of the bath is noted by means of a thermometer; S is a wide-mouthed vessel of strong glass, placed in the bath, which serves to receive the substance to be dried, contained in a glass tube as wide as practicable, and sealed at one end.

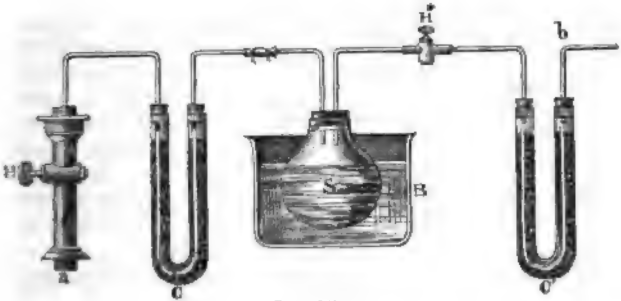

Fig. 35.

By working the air-pump, with the cork H open, the air in S is rarefied; by closing H, and opening H', the apparatus is filled with carbonic acid, freed from moisture in its passage through the chloride of calcium tube, c'.

By repeating this operation, the apparatus is filled completely with dry carbonic acid. H' is then closed, and the pump set to work. The oil-bath is then heated to the desired degree, carbonic acid being admitted, from time to time, through H'. With the carbonic acid pumped out, after closing the cork H', is removed also the moisture absorbed by it, which is retained in the chloride of calcium tube. The entire operation takes about an hour.

§ 31.

In technical and agricultural chemical processes, when it is required to dry a number of samples simultaneously at a higher temperature, the *drying-disk*, devised by me, and represented in Fig. 36, will be found very practical and convenient.

This apparatus consists, as the engraving shows, of a lathe-turned circular cast-iron plate, 37 mm. thick and 21 centimetres in diameter; the bulk of the plate is, therefore, not inconsiderable, the weight being 8 kilogrammes. Owing to this circumstance, the heat is very uniformly diffused through its entire mass, and it is easy to maintain it steadily at the desired temperature. The plate has six smooth-turned cylindrical cavities, placed round the centre, at equal distances from each other, in which six lathe-turned cylindrical brass pans, of 55 mm. diameter and 18 mm. height in the clear, are fitted somewhat loosely, to admit of their ready removal after the process of heating. The pans are provided with small handles, turned towards the periphery of the disk, and resting in appropriate grooves. Behind every cavity is stamped on the plate a number, from 1 to 6; the handles of the pans bear corresponding numbers, so that every pan has its own proper cavity. The distance from the centre of the plate to the centre of the pans is 6·5 centimetres; the rims of the pans are level with the surface of the plate. Five of the pans are intended to receive the samples (ores, parts of plants, &c.); the sixth receives the thermometer, to which end a brass ring is fitted into it, projecting 3 centimetres above the surface. The pan, which is thereby heightened, is filled with brass or copper filings, and the bulb of the thermometer immersed in these down to the bottom. The heat is made to act upon the centre of the plate.

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* *Fr. Rochleder*, "Journ. für prakt. Chemie," 66, 208.

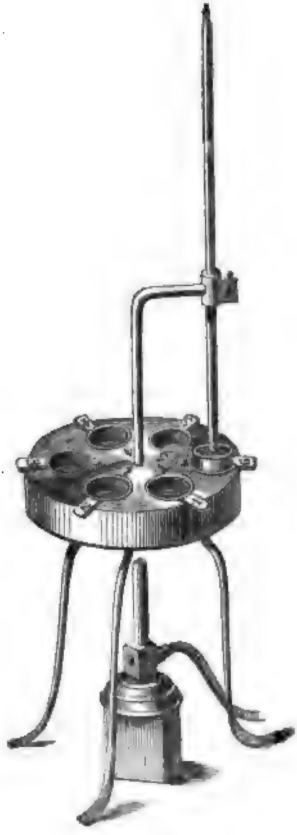

Fig. 36.

f. Substances which suffer no alteration at a red heat, such as sulphate of baryta, potash, &c., are very readily freed from moisture. They need simply be heated in a platinum or porcelain crucible over a gas- or spirit-lamp until the desired end is attained. The crucible, having first been allowed to cool a little, is put, still hot, under a desiccator, and finally weighed when cold.

III. General Procedure in Quantitative Analyses.

§ 32.

It is important, in the first place, to observe that we embrace in the following general analytical method only the analysis and quantitative estimation of the metals and their combinations with the metalloids, and the inorganic acids and salts. With respect to the quantitative analysis of other compounds, it is not easy to lay down a universally applicable method, except that their respective constituents usually require to be converted first into acids or bases, before their separation and quantitative estimation can be attempted; this is the case, for instance, with sulphide of phosphorus, chloride of sulphur, chloride of iodine, sulphide of nitrogen, &c.

As has already been observed before, the quantitative analysis of a substance presupposes an accurate knowledge of the nature and properties of the same, and of its several constituents; as this will enable the operator at once to decide whether the direct quantitative estimation of each individual constituent be necessary or not; and, consequently, whether he need operate only on one sample of the substance, or whether he has to determine in several different portions respectively, the relative amount of each individual constituent. Let us suppose, for instance, we have a mixture of chloride of sodium and anhydrous sulphate of soda, and wish to ascertain the exact proportion in which each of these two substances is contained in the mixture. Here it would be superfluous to determine separately the proportional amount of every individual constituent, since the determination either of the quantity of the chlorine, or of that of the sulphuric acid, is quite sufficient to answer the purpose; still the double estimation of both the chlorine and the sulphuric acid will afford us an infallible control for the correctness of our analysis; since the united weights of these two substances, added to the known proportion of their respective equivalents of sodium and soda, must be equal to the weight of the analysed portion of the mixture.

This double estimation may be made, in this instance, either in one and the same sample of the mixture, by first precipitating the sulphuric acid with nitrate of baryta, and subsequently the hydrochloric acid from the filtrate with solution of nitrate of silver; or a separate portion of the mixture may be appropriated to each of these two operations. The latter method, whenever it is at all applicable, is preferable to the former, in cases where we have to deal with perfectly homogeneous substances; and where we have a sufficient quantity of substance to act upon. It is more convenient than the former method, and leads to more accurate results; since, when operating upon one and the same sample of a substance, the unavoidable washing of the first precipitate swells the amount of liquid so considerably, that the analysis is thereby delayed, and, moreover, loss of substance less easily guarded against.

The student will always do well, at least in operations on a larger scale or of a more complex nature, to draw up a fixed, written plan, and to accurately note, during the entire process, every successive phase, with its results. To trust to memory, is most unwise; and to work without a maturely considered, fixed plan, is equally so. A mere unthinking and purposeless stringing together of a series of filtrations, evaporations, ignitions, and weighings is not chemistry, however well these several operations may be performed.

We will now proceed to describe the various operations constituting the process of quantitative analysis.

§ 33.

1. WEIGHING THE SUBSTANCE.

The amount of matter required for the quantitative analysis of a substance depends upon the nature of its constituents; it is, therefore, impossible to lay down rules for guidance on this point. Half a gramme of chloride of sodium, and even less, is sufficient to effect the estimation of the chlorine. For the quantitative analysis of a mixture of common salt and sulphate of soda, 1 gramme will suffice; whereas, in the case of ashes of plants, complex minerals, &c., 3 or 4 grammes, and even more, are required. The average quantity of substance required for the purposes of quantitative analysis may, accordingly, be said to range, in most cases, between 1 and 4 grammes. For the estimation of constituents present in very minute proportions only, as, for instance, alkalies in limestones, phosphorus or sulphur in cast-iron, &c., much greater quantities are often required—10, 20, 50, grammes, and more.

The greater the amount of substance operated upon, the more accurate will be the results of the analysis; the smaller the quantity, the less time will be required for the performance of the operation. We would advise the student to endeavor to combine accuracy with economy of time. The less substance he takes to operate upon, the more carefully he ought to weigh; the larger the amount of substance, the less harm can result from slight inaccuracies in weighing. For somewhat large quantities of substance, the accuracy of weighing may be safely limited to within about 1 milligramme; for minute quantities, to about $\frac{1}{10}$ of a milligramme.

If several different quantities of a substance are to be operated upon, the best way is to weigh off the several portions successively; which may be accomplished most readily by weighing in a glass tube, or other appropriate vessel of known weight, the whole amount of substance intended to be devoted to the analytical process. Out of this tube the portions required for the several operations are taken, and the weight is ascertained each time from the diminution in the weight of the tube.

The work may often also be materially lightened, by weighing off a larger portion of the substance, dissolving this in sufficient liquid to give exactly $\frac{1}{4}$, $\frac{1}{2}$ or a litre of solution, and taking out for the several estimations aliquot parts of the fluid, by means of a pipette of 50 c. c. or 100 c. c. capacity. The first and most essential condition of this proceeding, of course, is that the pipettes must accurately correspond with the measuring flasks. The method of ascertaining this fact has been described in § 18 and § 20. It may, however, be determined, also, in a more simple way, by emptying the pipettes 5 times, 10 times, &c., into the measuring flasks, and observing whether the volume thus poured in corresponds exactly with the line-mark of the flask.

§ 34.

2. ESTIMATION OF THE AMOUNT OF WATER CONTAINED IN A SUBSTANCE.

If the substance to be examined contains water, it is usual, in the great majority of cases, to begin by determining the amount of this water. This operation is generally simple; in some instances, however, it has its difficulties. This depends upon various circumstances, viz., whether the compounds intended for analysis yield their water readily or not; whether they can bear a red heat without suffering decomposition; or whether, on the contrary, they give off other volatile substances, besides water, even at a lower temperature.

The correct knowledge of the constitution of a substance depends frequently upon the accurate estimation of the quantity of water contained in it; in many cases—for instance, in the analysis of the salts of known acids—the estimation of the amount of water contained in the analysed compound suffices to enable us to deduce the formula. The estimation of the amount of water contained in a substance, is, therefore, one of the most important, as well as most frequently occurring operations of quantitative analysis. The proportion of water contained in a substance may be determined in two ways, viz., 1, from the diminution of weight consequent upon the expulsion of the water; 2, by weighing the amount of water expelled.

§ 35.

a. ESTIMATION OF THE WATER FROM THE LOSS OF WEIGHT CONSEQUENT UPON ITS EXPULSION.

This method, on account of its simplicity, is almost invariably resorted to in quantitative analyses, except in cases where it is inapplicable from the nature of the substance examined. The *modus operandi* depends upon the nature of the substance under examination.

α. The Substance bears a Red Heat, without losing other Constituents besides Water, and without absorbing Oxygen.

The substance is weighed in a platinum or porcelain crucible, which is then heated over the flame of a gas- or spirit-lamp, very gently at first, but increasing gradually to the desired point. When the crucible has been maintained some time at a red heat, it is removed from the flame, let cool a little, put still warm under the desiccator, and finally weighed when cold. The same operation is then repeated, and the weight again ascertained. If no further diminution of weight has taken place, the process is at an end, the desired object being fully attained. But if the weight is less than after the first heating, the operation must be repeated until the weight remains constant.

In the case of silicates, the heat must be raised to a very high degree, since many of them (*e.g.* talc, steatite, nephrite), begin only at a red heat to give off water, and require a yellow heat for the complete expulsion of that constituent. (*Th. Scheerer*, in Liebig and Kopp's "Annual Report" for 1851, 610.)

In the case of substances that have a tendency to puff up, or to spirt, a small glass flask may sometimes be advantageously substituted for the crucible. Care must be taken to remove the least traces of aqueous vapor from the vessel, by suction through a glass tube.

Decrepitating salts (chloride of sodium, for instance) are put—finely pulverized if possible—in a small covered platinum crucible, which is then placed in a large covered crucible, and a gentle heat applied, which is gradually increased to the requisite degree.

β. The Substance does not yield other Constituents besides Water, upon the application of a Red Heat; but it has a Tendency to absorb Oxygen (as many salts of Protoxide of Iron, for instance).

The substance is put into the bulb of a bulb-tube, made of difficultly fusible glass, and gradually heated to redness, whilst a slow current of carbonic acid gas, dried previously by transmission through sulphuric acid, is kept passing through the tube; the substance is maintained at a red heat, until the complete expulsion of the water is accomplished; it is then allowed to cool in the bulb, the transmission of the carbonic acid gas being continued all the while; when cold, the substance is weighed. When employing this method, it is always advisable to collect the expelled water in a chloride of calcium tube, connected with the bulb-tube by means of a perforated cork, and to weigh this before and after, by way of control. (Compare § 36.)

Vohl has lately recommended[*] to estimate the water in substances of this kind by mixing them in a tared platinum or porcelain crucible, with a weighed quantity, in excess, of pure bichromate of potassa, thoroughly freed from water by fusion at a gentle heat, adding some water, evaporating cautiously, drying at 392° F., and calculating the amount of water by the diminution of weight. This method, certainly, will give, in many cases, satisfactory results; but it does not appear to me to excel the other method either in accuracy or simplicity. It is quite inapplicable, of course, in presence of organic substances, or of ammoniacal salts. Neutral chromate of potassa must be substituted for the acid salt, in cases where the application of the former would be attended with evolution of oxygen or chlorine, as, for instance, in the estimation of the water in salts of protoxide of iron containing chloric acid or sulphuric acid.

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[*] "Annal. der Chem. u. Pharm." 94, 216.

γ. *The Substance loses other Constituents besides Water, upon the Application of a Red Heat (Carbonic Acid, Sulphuric Acid, Fluoride of Silicon, &c.).*

Here the analyst has to consider, in the first place, whether the water may not be expelled at a lower degree of heat, which does not involve the loss of other constituents. If this may be done, the substance is heated either on the water-bath, or where a higher temperature than 212° F. is required, in the air-bath or oil-bath, the temperature being regulated by the thermometer. The expulsion of the water may be promoted, if necessary or desirable, by the co-operation of a current of air (compare § 29 and § 30); or by the addition of pure dry sand to the substance, to keep it porous ("Ann. der Chemie und Pharm." 53, 233). The process must be continued under these circumstances also, until the weight remains constant.

In cases where, for some reason or other, a degree of heat below redness is insufficient to effect the purpose in view, the analyst has to consider whether the desired end may not be attained at a red heat, by adding some substance that will retain the volatile constituent whose loss is apprehended. Thus, for instance, the crystallized sulphate of alumina loses at a red heat, besides water, also sulphuric acid; now, the loss of the latter constituent may be guarded against, by adding to the sulphate an excess (about six times the quantity) of finely pulverized, recently ignited, pure oxide of lead. But the addition of this substance will not prevent the escape of fluoride of silicon from silicates when exposed to a red heat (*List*, "Ann. d. Chemie und Pharm." 81, 189).

The amount of water in iodine of commerce may be determined by triturating the iodine together with eight times the quantity of mercury, and drying the mixture at 212° F. (*Bolley*, Dingler's "Polytechnic Journal," 126, 39.)

δ. *The Substance contains several differently combined Equivalents of Water which requires different Degrees of Temperature for Expulsion.*

Substances of this nature are heated first in the water-bath, until their weight remains stationary; they are then exposed in the oil- or air-bath to temperatures of 302°, 392°, or 482° F., &c., successively; and finally heated to redness over the flame of a gas- or spirit-lamp.

In this manner differently combined equivalents of water may be distinguished, and their respective quantities correctly estimated. Thus, for instance, crystallized sulphate of copper contains 28·87 per cent. of water, which escapes at a temperature below 282° F., and 7·22 per cent., which escapes only at a temperature between 428° and 500° F. It is often advisable to assist the action of heat by rarefication of the air. Thus sulphate of magnesia, when dried *in vacuo*, over sulphuric acid, loses at 212° F. 5 equivalents of water; dried in the air at 269·6° F., it loses the sixth, and at a moderate red heat, the seventh equivalent of water.

§ 36.

b. Estimation of Water by Expulsion and Direct Weighing.

This method is resorted to in the case of substances which, upon ignition, lose, besides water, other constituents, which cannot be retained even by the addition of some other substance (*e.g.* carbonic acid, oxygen); and sometimes also to control and verify the results obtained by one of the methods described sub *a*. The principle of the method is to expel the water by the application of a red heat, so as to admit of the condensation of the aqueous vapor, and the collection of the condensed water in an appropriate apparatus, partly in the direct way, partly by the agency of some hygroscopic substance. The increase in the weight of this apparatus represents the quantity of the water expelled.

The operation may be conducted in various ways; the following, however, is one of the most appropriate:—

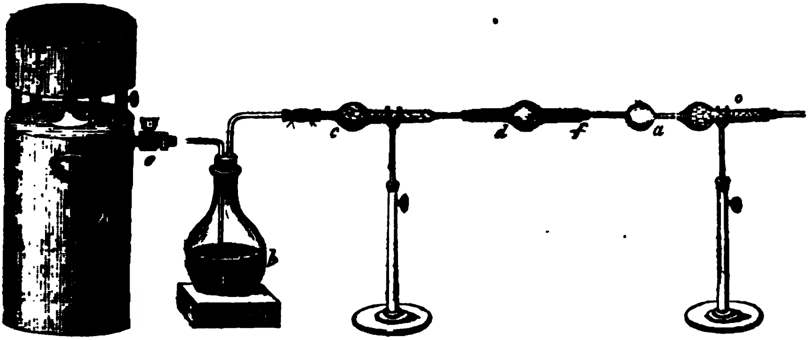

Fig. 37.

B represents a gasometer filled with air; *b* a flask half filled with concentrated sulphuric acid; *c* and *a o* are chloride of calcium tubes; *d* is a glass tube expanded in the middle into a bulb.

The substance intended for examination is accurately weighed in the perfectly dry tube *d*, which is then connected with *c* and the accurately weighed chloride of calcium tube *a o*, by means of sound and well-dried perforated corks.

The operation is commenced by opening the stop-cock *e* a little, to allow the air, which loses all its moisture in its passage through *b* and *c*, to pass slowly through *d*; the tube *d* is then heated to beyond the boiling-point of water, by the application of the flame of a spirit-lamp at the point *f*, taking care, always, not to burn or singe the cork; and finally, the bulb *d*, which contains the substance, is exposed to a low red heat, the temperature at *f* being maintained meanwhile at the point indicated. When the expulsion of the water has been accomplished, the air is allowed to pass a few instants longer through the apparatus, which is then disconnected, and the chloride of calcium tube *a o* accurately weighed when cold. The increase in the weight of this tube represents the quantity of water originally present in the substance examined.

The empty bulb *a*, in which the greater portion of the water collects, has not only for its object to prevent the liquefaction of the chloride of calcium, but enables the analyst also to test the condensed water as to its reaction and purity.

The apparatus may, of course, be modified in various ways; thus, the chloride of calcium tubes may be bent in the form of the letter U; a tube of the same form, filled with pieces of pumice-stone saturated with sulphuric acid, may be substituted for the flask with sulphuric acid; and an aspirator (Fig. 29) joined to *o*, for the gasometer.

The expulsion of the aqueous vapor from the tube containing the substance under examination, into the chloride of calcium tube, may be effected also by other means than a current of air supplied by a gasometer or aspirator; viz., the substance under examination may be heated to redness in a perfectly dry tube, together with carbonate of lead, since the carbonic acid of the latter, escaping at a red heat, serves here the same purpose as a stream of air. This method is principally applied in cases where it is desirable to retain an acid which otherwise would volatilize together with the water; thus, it is applied, for instance, for the direct estimation of the water contained in the bisulphate of potassa, &c.

Fig. 38.

Fig. 38 represents the apparatus used for the application of this method. *a b* is a common combustion furnace; *c f'* a tube filled from *c* to *d* with carbonate of lead, which has first been heated to incipient decomposition, then cooled in a close tube; from *d* to *e* is placed the substance to be analysed, intimately mixed with carbonate of lead; and from *e* to *f* again pure carbonate of lead. The chloride of calcium tube *g*, being accurately weighed, is connected with the tube *c f'*, by means of a well-dried perforated cork, *f'*.

The operation is commenced by surrounding the tube *c f'* with red-hot charcoal, advancing from *f'* towards *c*; the fore part of the tube which protrudes from the furnace should be maintained at a degree of heat which barely permits the operator to lay hold of it with his fingers. All further particulars of this operation will be found in the chapter on organic elementary analysis. The mixing of the carbonate of lead with the substance to be analysed is performed best in the tube with a piece of wire. The tube *c f'* may be short and narrow.

The foregoing methods for the direct estimation of water do not, however, yet embrace all cases in which those described in § 35 are inapplicable; since they can be employed with success only if the substances escaping along with the water are such as will not wholly or partly condense in the chloride of calcium tube, or in a hydrate of potassa tube, or one filled with pumice-stone saturated with sulphuric acid, which might be used instead. Thus they are perfectly well adapted for determining the amount of water in the basic carbonate of zinc, but they cannot be applied to determine the amount of water in sulphate of soda and ammonia. With substances like the latter, we must either have recourse to the processes of organic elementary analysis, or we must rest satisfied with the indirect estimation of the water.

§ 37.

3. SOLUTION OF SUBSTANCES.

Before pursuing the analytical process further, it is in most cases necessary to dissolve the substance under examination. This operation is simple where the substance to be analysed may be dissolved by the direct action of water, or acids, or alkalies, &c., upon it; but it is more complicated in cases where we have to operate upon substances requiring fluxing as an indispensable preliminary to their solution.

When we have mixed substances to operate upon, the component parts of which behave differently with solvents, it is not by any means necessary to dissolve the whole substance; on the contrary, the separation may, in such cases, be effected, in the most simple and expeditious manner, by the successive application of the different solvents required. Thus, for instance, a mixture of nitrate of potassa, carbonate of lime, and sulphate of baryta, may be readily and accurately separated by dissolving out, in the first place, the nitrate of potassa with water, and subsequently the carbonate of lime by hydrochloric acid, leaving the insoluble sulphate of baryta.

§ 38.

a. DIRECT SOLUTION.

The direct solution of substances is effected, according to circumstances, either in beakers, or in flasks or dishes, and may, if necessary, be promoted by the application of heat; for which purpose the water-bath will be found most convenient. In cases where an open fire, or the sand-bath is resorted to, the analyst must take care to guard against actual ebullition of the fluid, since this would render it next to impossible to avoid loss of substance from spirting, especially in cases where the process is conducted in a dish. Fluids containing a sediment, either insoluble, or, at least, not yet dissolved, will, when heated over the lamp, often spirt even at temperatures far short of the boiling-point.

In cases where the solution of a substance is attended with evolution of gas, the process is conducted in a flask, placed in a sloping position, so that the spirting drops may be thrown against the walls of the vessel, and thus secured from being carried off with the stream of the evolved gas; or it may be conducted in a beaker, covered with a large-sized watch-glass or porcelain dish, which, after the solution is effected, and the gas expelled by heating on the water-bath, must be thoroughly rinsed with the washing bottle.

In cases where the solution has to be effected by means of concentrated volatile acids (hydrochloric acid, nitric acid, aqua regia), the operation should never be conducted in a dish, but always in a flask covered with a watch-glass, or placed in a slanting position, and the application of too high a temperature be carefully avoided. The operation should always be conducted also under a hood or chimney, with proper draught, to carry off the escaping acid vapors. In my own laboratory, I use for the latter purpose the following simple contrivance: a leaden pipe, permanently fixed in a convenient position, leads from the working table through the wall or the window-frame into the open air. The end in the laboratory is connected with one of the mouths of a two-necked bottle, which contains a little water. The other mouth of the bottle is closed with a perforated cork, bearing a firmly-fixed glass tube bent at a right angle; the portion of the tube which enters the bottle must not dip into the water. The solution-flask being now closed with a perforated cork, or an india-rubber cap, bearing a glass tube, connected by means of india-rubber, with the bent tube in the double-necked bottle, the vapors evolved are carried out of the laboratory without the least inconvenience to the operator; moreover, no receding of the vapors upon cooling need be apprehended. Instead of conveying the vapors away through a tube leading into the open air, a conical glass-tube filled with pieces of broken glass, which are moistened with water or solution of carbonate of soda, may be put over the second mouth of the double-necked bottle. I, however, prefer the other method. In some cases, it is advisable also to conduct the escaping vapors into a little water, and, when solution has been effected, make the water recede by withdrawing the lamp, since this will, at the same time, serve to dilute the solution; care must be taken, however, to guard against a premature receding of the water in consequence of an accidental refrigeration of the solution flask.

It is often necessary, in conducting a process of solution, to guard against the action of the atmospheric oxygen; in such cases, a slow stream of carbonic acid is transmitted through the solution-flask; in some cases, the air may be expelled also, by simply first introducing a little bicarbonate of soda into the flask containing the substance to be dissolved and an excess of acid.

§ 39.

b. SOLUTION, PRECEDED BY FLUXING.

Substances insoluble in water, acids, or aqueous solutions of alkalies, usually require decomposition by fluxing, to prepare them for analysis. Substances of this kind are often met with in the mineral kingdom; most silicates, the sulphates of the alkaline earths, chrome ironstone, &c., belong to this class.

The object and general features of the process of fluxing have already been treated upon in the qualitative part of the present work. The special method of conducting this important operation will be described hereafter in the chapter on the analysis of silicates, and in the proper place; as a satisfactory description of the process, with its various modifications, cannot well be given without entering more minutely into the particular circumstances of the several special cases.

Decomposition by fluxing often requires a higher temperature than is attainable with a spirit-lamp with double draught, or with a common gas-lamp. In such cases, the glass-blower's* lamp, fed with gas, is used with advantage.

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* Griffin, Bunhill-row, supplies these lamps.

§ 40.

4. CONVERSION OF THE DISSOLVED SUBSTANCE INTO A PONDERABLE FORM.

The conversion of a substance in a state of solution into a form adapted for weighing may be effected either by *evaporation* or by *precipitation*. The former of these operations is applicable only in cases where the substance the weight of which we are desirous to ascertain either exists already in the solution in the form suitable for the determination of its weight, or may be converted into such form by evaporation in conjunction with some re-agent. The solution must, moreover, contain the substance unmixed, or, at least, mixed only with such bodies as are expelled by evaporation or at a red-heat. Thus, for instance, the amount of sulphate of soda present in an aqueous solution of that substance may be ascertained by simple evaporation; whilst the carbonate of potassa contained in a solution had always better be converted into chloride of potassium, by mixing the fluid with solution of chloride of ammonium, and evaporating the mixture.

Precipitation may always be resorted to whenever the substance in solution admits of being converted into a state or combination in which it is insoluble in the menstruum.

§ 41.

a. EVAPORATION.

In processes of evaporation for pharmaceutical or technico-chemical purposes the principal object to be considered is saving of time and fuel; but in evaporating processes in quantitative analytical researches this is merely a subordinate point, and the analyst has to direct his principal care and attention to the means of guarding against loss or contamination of the substance operated upon.

The simplest case of evaporation is when we have to *concentrate a clear fluid, without carrying the process to dryness.* To effect this object, the fluid is poured into a basin of sufficient size to hold at least one-third more than the quantity of fluid to be operated on. Heat is then applied by placing the basin either on the water-bath or sand-bath, or on a common stove, or over the flame of a gas- or spirit-lamp, care being taken always to guard against actual ebullition, as this invariably and unavoidably leads to loss in form of small drops of fluid

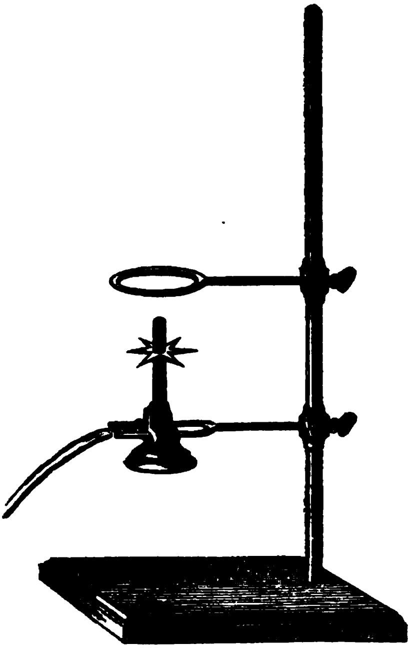

Fig. 39.

spirting out. Evaporation over a gas- or spirit-lamp, when conducted with proper care, is an expeditious and cleanly process. *Bunsen's* gas-lamp (see Fig. 39), which has already been described in the "Qualitative Analysis," may be used most advantageously in operations of this kind; a little wire-gauze cap, loosely fitted upon the tube of the lamp, is a material improvement. By means of this simple arrangement it is easy to produce even the smallest flame, without the least apprehension of ignition of the gas within the tube.

If the evaporation is to be effected on the water-bath, and the operator happens to possess a Beindorf, or other similarly-constructed steam apparatus, the evaporating-dish, or pan, may be placed simply into one of the openings corresponding to its size. Otherwise recourse must be had to the water-bath illustrated by Fig. 40.

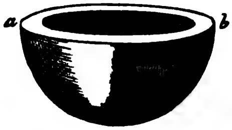

Fig. 40.

The engraving represents a basin made of strong sheet copper. This basin is half filled with water, which is kept boiling over the flame of a gas-, spirit-, or oil-lamp. Rings adapted to the different sizes of the evaporating-dishes serve to receive the latter. The diameter of the vessel from *a* to *b* should be from 12 to 18 centimetres.

It will occasionally happen that the water in the bath completely evaporates without the operator being aware of it; this is a great inconvenience, as it will often occur, in such cases, that residues are heated to a higher degree than desirable; that concentrated solutions

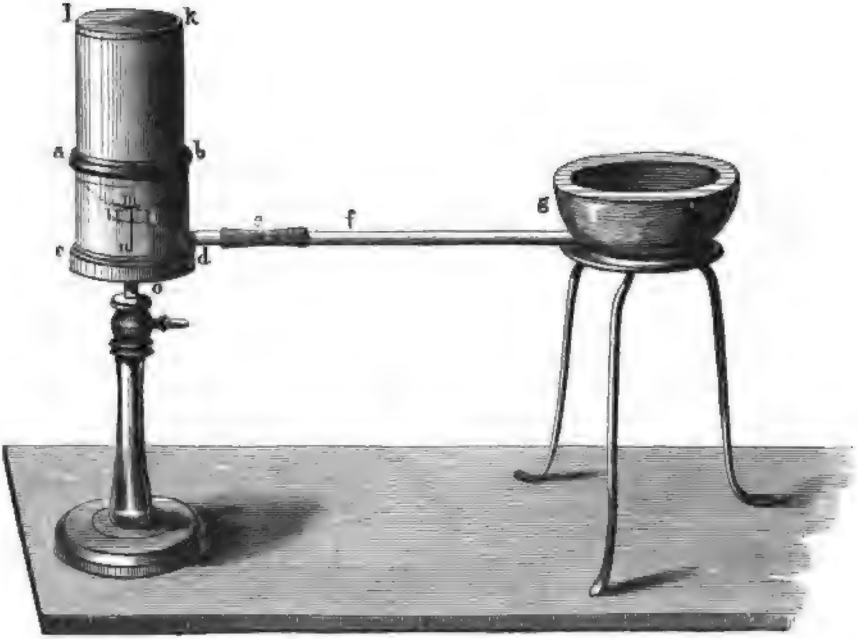

Fig. 41.

spirt, &c. I have, therefore, lately constructed, for my own laboratory, a water-bath with constant level (see Fig. 41).

The apparatus consists of a zinc vessel, *a b c d*, 10 centimetres high, 12 centimetres in diameter; this is connected with the water-bath, *g*, by means of india-rubber, *e*, and a copper tube, *f*. A bottle, *h i k l*, made of sheet zinc, and filled with water, is inverted into the vessel *a b c d*; the cylindrical part of the bottle measures 17 centimetres in height, the diameter of the neck 3 centimetres; the true orifice of the bottle, which is 15 mm. wide, is at the beginning of the neck; this orifice is closed by a valve, *m*. Upon inverting the bottle into *a b c d*, the wire *n*, striking upon the bottom of the vessel, pushes open the valve. By raising or lowering the pillar-support *o*, upon which the vessel *a b c d* rests, it is easy to establish any desired level in *g*, which will remain unaltered so long as there is any water left in the bottle. The tube *f* is bent downward in the water-bath nearly to the bottom.

If the operator can conduct his processes of evaporation in a private room, where he may easily guard against any occurrence tending to suspend minute particles of dust, &c., in the air, he will find it no very difficult task to keep the evaporating fluid clean; and he may, therefore, safely leave the dishes, or pans, uncovered, which, in that case, is the best mode of proceeding.* But in a large laboratory, frequented by many people, or in a room exposed to draughts of air, or in which coal fires are burning, the greatest caution is required to protect the evaporating fluid from contamination by dust or ashes.

For this purpose the evaporating dish is either covered with a sheet of filtering-paper turned down over the edges, or a glass rod twisted into a triangular shape (Fig. 21) is laid upon it, and a sheet of filtering-paper spread over it, which is kept in position by a glass rod laid across, the latter again being kept from rolling down by the slightly turned up ends, *a* and *b*, of the triangle.

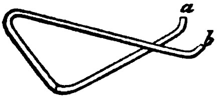

Fig. 42.

The best way, however, is the following:—Take two small thin wooden hoops (Fig. 43), one of which fits loosely in the other; spread a sheet of blotting-paper over the smaller of the two, and push the larger one over it. This forms a cover admirably adapted to the purpose; and, whilst in no way interfering with the operation, it completely protects the evaporating fluid from particles of dust floating in the air, and may be readily taken off; the paper cannot dip into the fluid; the cover lasts a long time, and may, moreover, at any time be easily renewed.

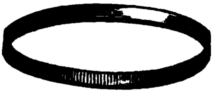

Fig. 43.

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* In my own laboratory, evaporating processes in quantitative researches are conducted in separate closets. Those closets are the best, the floor and roof of which are constructed of slabs of sandstone, and the walls of bricks, lined with gypsum cement, properly smoothed. At the topmost part of the back wall is a horizontal channel of sufficient width, which at a short distance opens into a separate Russian chimney. No fire must ever be made under this chimney; but it is most desirable to have it placed quite close to another chimney, kept constantly warm by some source of heat, that of the steam apparatus, for instance, as this will, in that case, serve also to keep warm the Russian chimney, which is intended to carry off the vapor. The front wall of the evaporating closet is formed of sandstone pillars eighteen decimetres high, in which are fitted sliding-windows with wooden frames.

It must be borne in mind, however, that the common filtering paper contains always certain substances soluble in acids, such as lime, sesquioxide of iron, &c., which, were covers of the kind just described used over evaporating dishes containing a fluid evolving acid vapors, would infallibly dissolve in these vapors, and the solution dripping down into the evaporating fluid, would speedily contaminate it. Care must be taken, therefore, to use only such filtering paper as has been freed by washing from the presence of substances soluble in acids.

Evaporation for the purpose of concentration may be effected also in glass flasks; these are only half filled, and placed in a slanting position. The process may be conducted on the sand-bath, or over the flame of a gas- or spirit-lamp, or even, and with equal propriety, over a charcoal fire. In cases where the operation is conducted over a lamp or a charcoal fire, it is the safest way, to place the flasks on wire gauze. Gentle ebullition of the fluid can do no harm here, since the slanting position of the flask guards effectively against risk of loss from the spirting of the liquid.

The evaporation of fluids containing an insoluble sediment is best conducted on the water-bath; since on the sand-bath, or over the flame of a lamp, it is next to impossible to guard against loss from spirting, occasioned by slight explosions of steam bubbles, arising from the sediment impeding the equal diffusion of the heat. Still there remains another, though less safe way, viz., to conduct the evaporation in a crucible placed in a slanting position over the flame, as illustrated in Fig. 44. In this process, the flame is made to play upon the crucible above the level of the fluid.

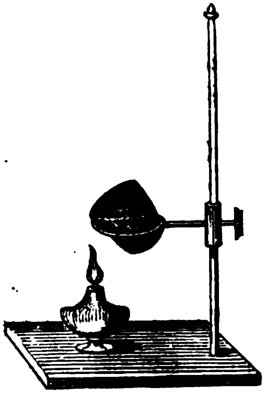
Fig. 44.

Where a fluid has to be evaporated to absolute dryness, as is so often the case, the operation should always, if possible, be terminated on the water-bath. In cases where the nature of the dissolved substance precludes the application of the water-bath, the object in view may often be most readily attained by heating the contents of the evaporating-dish from the top, which is effected by placing the dish in a proper position in a drying case, or closet, of which the upper plate is heated by a flame (that of the water- or sand-bath) passing over it.

In cases where the heat has to be applied from the bottom, a method must be chosen which admits of an equal diffusion and ready regulation of the heat. An air-bath is well adapted for this purpose;* the apparatus illustrated in Fig. 40 may be used, although I must not omit to mention, that this mode of application will in the end seriously injure it. If the operation has to be conducted over the flame of a lamp, the dish should be placed high above the flame; best on wire gauze, since this will greatly contribute to an equal diffusion of the heat. The use of the sand-bath is objectionable here, because with that apparatus we cannot reduce the heat so speedily as may be desirable. But no matter which method or apparatus be employed, *this* rule applies equally to all of them: that the operator must watch the process, from the moment that the residue begins to thicken, in order to prevent spirting, by reducing the heat, and breaking the pellicles and crusts which form on the surface, with a glass rod, or a platinum wire or spatula.

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* Taylor's air-bath will be found very useful.

Saline solutions that have a tendency, upon their evaporation, to ascend along the sides of the vessel, and may thus finally pass over the brim of the latter, which, of course, involves the risk of a loss of substance, should be heated from the top, in the way just indicated; since by that means the sides of the vessel will get heated sufficiently to cause the instantaneous evaporation of the ascending liquid, preventing thus its overflowing the brim. The inconvenience just alluded to may, however, be obviated also, in most cases, by covering the brim, and the uppermost part of the inner side of the vessel, with a very thin coat of tallow, thus diminishing the adhesion between the fluid and the vessel.

In the case of liquids evolving gas bubbles upon evaporating, particular caution is required to guard against loss from spirting. The safest way is to heat such liquids in an obliquely-placed flask, or in a beaker-glass covered with an evaporating dish; the latter is removed as soon as the evolution of gas bubbles has ceased, and the fluid that may have spirted up against it, is carefully rinsed into the glass, by means of a washing-bottle. If the evaporation has to be conducted in the common way, in a dish, a rather capacious one should be selected, and a very moderate degree of heat applied at first, and until the evolution of gas has nearly ceased.

If a fluid has to be evaporated *with exclusion of air*, the best way is to place the dish under the bell of an air-pump, over a vessel with sulphuric acid, and to exhaust; or a tubulated retort may be used, with a long tube fixed into it, reaching down to near the surface of the liquid, and through which hydrogen or carbonic acid gas is transmitted.

The respective materials of the evaporating vessels may exercise a much greater influence on the results of an analysis than is generally believed. Many rather startling phenomena that are observed in analytical processes may arise simply from the evaporated liquid having dissolved particles of the material of the evaporating vessel; this must, of course, lead also to great errors in the results of the analysis.

The importance of this point has induced me to subject it to a new and searching investigation (see Appendix, Analytical Notes and Experiments, 1—4), of which I will here briefly intimate the results.

Distilled water kept boiling for some length of time in flasks of Bohemian glass, dissolves very appreciable traces of that material. This is owing to the formation of soluble silicates; the particles dissolved consist chiefly of potassa, or soda and lime, in combination with silicic acid. A much larger proportion of the glass is dissolved by water containing caustic or carbonated alkali; boiling solution of chloride of ammonium also strongly attacks glass vessels. Boiling dilute acids, with the exception, of course, of hydrofluoric and hydrofluosilicic acids, exercise a less powerful solvent action on glass than pure water. Porcelain (Berlin dishes) is much less affected by water than glass; alkaline liquids also exercise a much less powerful solvent action on porcelain than on glass; the quantity dissolved is, however, still notable. Solution of chloride of ammonium acts on porcelain as strongly as on glass; dilute acids, though exercising no very powerful solvent action on porcelain, yet attack that material more strongly than glass. It results from these data, that in analyses pretending to a high degree of accuracy, platinum and silver dishes should always be preferred. The former may be used in all cases where no free chlorine, bromine, or iodine is present in the fluid, or can be formed in the course of the process of evaporation. Fluids containing caustic alkalies may safely be evaporated in platinum, but not to the point of fusion of the residue. Silver vessels should never be used to evaporate acid fluids nor liquids containing alkaline sulphides; but they are admirably suited for evaporating solutions of caustic and carbonated alkalies, as well as of most neutral salts.

§ 42.

We come now to *weighing the residues remaining upon the evaporation of fluids.* We allude here simply to such as are soluble in water; those which are separated by filtration will be treated of in the next paragraph (Precipitation). Residues are generally weighed in the same vessel in which the evaporation has been completed, for which purpose platinum dishes, from 4 to 8 centimetres in diameter, provided with light covers, or large platinum crucibles, are best adapted, since they are lighter than porcelain vessels of the same capacity.

However, in most cases, the amount of liquid to be evaporated is too large for so small a vessel, and its evaporation in portions would occupy too much time. The best way, in cases of this kind, is to concentrate the liquid first in a larger vessel, and to terminate the operation afterwards in the smaller weighing vessel.

In transferring the fluid from the larger to the smaller vessel, the lip of the former is slightly greased, and the liquid made to run down a glass rod. (See Fig. 45).

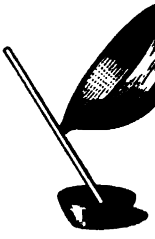

Fig. 45.

Finally the large vessel is carefully rinsed with a washing-bottle, until a drop of the last rinsing leaves no longer a residue upon evaporation on a platinum knife. When the fluid has thus been transferred to the weighing vessel, the evaporation is completed on the water-bath, and the residuary substance finally exposed to a red-heat, always provided, of course, it will admit of this process. For this purpose the dish is covered with a lid of thin platinum, or a thin glass plate, and then placed high over the flame of a lamp, and heated very gently until all the water which may still adhere to the substance is expelled; the dish is now exposed to a stronger, and finally to a red-heat. Where a glass plate is used to cover the vessel, this must, of course, be first removed before the application of red-heat can be resorted to. The dish is then allowed to cool; if the contents are liable to absorb water, the process of cooling must be conducted under a bell-glass, over a vessel containing concentrated sulphuric acid. (See Fig. 22.) After cooling, the covered dish is weighed with its contents. When operating upon substances which decrepitate, such as chloride of sodium, for instance, it is advisable to expose them—after their removal from the water-bath, and previously to the application of a naked flame—to a temperature somewhat above 212° F., either in the air-bath, or on a sand-bath, or on a common stove.

If the residue does not admit of the application of a red-heat, as is the case, for instance, with organic substances, ammoniacal salts, &c., the residuary mass is simply dried, at a temperature suited to its nature. In many cases, the temperature of the water-bath is sufficiently high for this purpose, for the drying of chloride of ammonium, for instance; in others, the air-bath or oil-bath must be resorted to. (See § 29 and § 30.) Under any circumstances, the desiccation must be continued until the substance ceases to suffer the slightest diminution in weight, after renewed exposure to heat, for from fifteen to thirty minutes. The dish should invariably be covered during the process of weighing.

If, as will frequently happen, we have to deal with a fluid containing a small quantity of a salt of potassa or soda, the weight of which we want to ascertain, in presence of a comparatively large amount of a salt of ammonia, which has been mixed with it in the course of the analytical process, I prefer the following method. The saline mass is thoroughly dried, in a large dish, on the water-bath, or, towards the end of the process, at a temperature somewhat exceeding 212° F. The dry mass is then, with the aid of a platinum spatula, transferred to a small glass dish, which is put aside for a time under a desiccator. The last traces of the salt left adhering to the sides and bottom of the large dish are rinsed off with a little water into the smaller dish, or the large crucible, in which it is intended to weigh the salt; the water is then evaporated, and the dry contents of the glass dish are added to the residue in the weighing dish or crucible: the ammonia salts are now expelled by the application of a red-heat, and the residuary fixed salts finally weighed. Should some traces of the saline mass adhere to the smaller glass dish, they ought to be removed and transferred to the weighing vessel, with the aid of a little pounded chloride of ammonium, or some other salt of ammonia, as the moistening again with water would involve an almost certain loss of substance.

§ 43

b. PRECIPITATION.

Precipitation is resorted to in quantitative analysis far more frequently than evaporation, since it serves not merely to convert substances into forms adapted for weighing, but also, and more especially, to separate them from one another. The principal intention in precipitation, for the purpose of quantitative estimations, is to convert the substance in solution into a form in which it is insoluble in the menstruum present. The result will, therefore, *cæteris paribus,* be the more accurate, the more the precipitated body deserves the epithet *insoluble,* and in cases where a substance may be precipitated in several different forms, possessing all the same degree of insolubility, *that* form will be the least liable to loss in which the smallest amount of liquid is required.

Hence it follows, first, that in all cases where other circumstances do not interfere, it is preferable to precipitate substances in their most insoluble form; thus, for instance, baryta had better be precipitated as sulphate than as carbonate; secondly, that when we have to deal with precipitates that are not quite insoluble in the menstruum present, we must endeavor to remove that menstruum, as far as practicable, by evaporation; thus a dilute solution of strontia should be concentrated, before proceeding to precipitate the strontia with sulphuric acid; and, thirdly, that when we have to deal with precipitates slightly soluble in the liquid present, but altogether insoluble in another menstruum, into which the former may be converted by the addition of some substance or other, we ought to endeavor to bring about this modification of the menstruum. Thus, for instance, alcohol may be added to water, to induce complete precipitation of chloride of platinum and ammonium, chloride of lead, sulphate of lime, &c.; thus again, the basic phosphate of magnesia and ammonia may be rendered insoluble in an aqueous menstruum by adding ammonia to the latter, &c.

Precipitation is generally effected in beakers. In cases, however, where we have to precipitate from fluids in a state of ebullition, or where the precipitate requires to be kept boiling for some time with the menstruum, flasks or dishes are substituted for beakers, with due regard always to the material of which they are made (see Evaporation, § 41, at the end).

The separation of precipitates from the fluid in which they are suspended, is effected either by *decantation* or *filtration*, or by both these processes jointly. But, before proceeding to the separation of the precipitate by any of these methods, the operator must know whether the precipitate is completely formed. To determine this most important point, an accurate knowledge of the properties of the various precipitates must be attained, which we shall endeavor to supply in the third section. As a general rule, the precipitated liquid should be allowed to stand at rest for several hours, before proceeding to the separation of the precipitate. This rule applies more particularly to crystalline, pulverulent, and gelatinous precipitates, whilst curdy and flocculent precipitates, more particularly when thrown down by boiling, may often be filtered off immediately. However, we must observe here, that all general rules, in this respect, are of very limited application.

§ 44.

a. SEPARATION OF PRECIPITATES BY DECANTATION.

When a precipitate subsides so completely and speedily in a fluid that the latter may be decanted off perfectly clear; or drawn off with a syphon, or removed by means of a pipette, and that the washing of the precipitate does not require a very long time, decantation is resorted to for its separation; this is the case, for instance, with chloride of silver, metallic mercury, &c.

Decantation will always be found a very expeditious and accurate method of separation, if the process be conducted with due care; it is necessary, however, in most cases, to promote the speedy and complete subsidence of the precipitate; and it may be laid down as a general rule, that heating the precipitate with its menstruum will produce the desired effect. Nevertheless, there are instances in which the simple application of heat will not cause the precipitate to subside so speedily and completely as may be desirable; in some cases, as with chloride of silver, for instance, agitation of the fluid must be resorted to; in other cases, some re-agent or other is to be added—hydrochloric acid, for instance, in the precipitation of mercury, &c. We shall have occasion, subsequently, in the fourth section, to discuss this point more fully, when we shall also treat of the vessels best adapted for the performance of this process in its various modifications, according to the nature of the precipitate.

After having washed the precipitate repeatedly with fresh quantities of the proper fluid, until there is no trace of a dissolved substance to be detected in the last rinsings, it is placed in a crucible or dish, if not already in a vessel of that description; the fluid still adhering to it is poured off as far as practicable, and the precipitate is then, according to its nature, either simply dried, or heated to redness.

A far larger amount of water being required for washing precipitates separated by decantation than is the case with those washed upon filters, the former process can be expected to yield *accurate* results only in cases where the précipitates are *absolutely insoluble.* For the same reasons, decantation is not ordinarily resorted to in cases where, besides the amount of the precipitated substance, we have to determine the amount of other constituents contained in the decanted fluid.

The decanted fluid must be allowed to stand at rest from twelve to twenty-four hours, to make quite sure that it no longer contains the minutest trace of the precipitated substance; if, after the lapse of twelve or twenty-four hours, according to circumstances, not a trace of precipitate is to be discovered, the fluid may be thrown away, except, of course, it should happen to be required for other purposes; but if a precipitate has subsided, this had better be estimated by itself, and the weight added to the gross amount; the precipitate may, in such cases, be separated from the supernatant fluid by decantation, or by filtration.

§ 45.

β. SEPARATION OF PRECIPITATES BY FILTRATION.

This operation is resorted to whenever decantation is impracticable, and, consequently, in the great majority of cases; provided always the precipitate is of a nature to admit of its being completely freed, by mere washing on the filter, from all foreign particles adhering to it. Where this is not the case, more particularly, therefore, with gelatinous precipitates, hydrate of alumina for instance, the combined operations of decantation and filtration are resorted to (§ 48).

aa. FILTERING APPARATUS.

Filtration, as a process of quantitative analysis, is almost exclusively effected by means of paper filters supported upon glass funnels.

Plain circular filters are most generally selected; plaited filters are only occasionally used. Much depends upon the quality of the paper. Good filtering paper must possess the three following properties:—1. It must completely retain the finest precipitates; 2. It must filter rapidly; and 3. It must be as free as possible from any admixture of inorganic bodies, but more especially from such as are soluble in acid or alkaline fluids.

It is a matter of some difficulty, however, to procure paper fully answering these conditions. The best is *Swedish filtering paper;* it bears the name, *J. H. Munktell,* in the watermark; and even this answers the purpose only so far as the first two conditions are concerned, but is by no means sufficiently pure for very accurate analyses, since it leaves upon incineration about 0·3 per cent. of ash,* and yields to acids perceptible traces of lime, magnesia, and sesquioxide of iron. It is always advisable, therefore, to treat even the Swedish filtering paper, when intended for use in minute and accurate investigations, with dilute hydrochloric acid, in order to free it from inorganic matter; after this process, the paper is carefully washed with water, to remove all traces of acid, and dried. In the case of very fine filtering paper, the best way to perform this operation, is to place the ready cut filters, either singly, or several together, in a funnel, exactly the same way as if intended for immediate filtration; they are then moistened with a mixture of one part of pure hydrochloric acid with two parts of water, which is allowed to act on them for about ten minutes; after this, all traces of the acid are carefully removed by washing the filters in the funnel repeatedly with warm water. The funnel being then covered with a piece of paper, turned over the edges, is put in a warm place until the filters are dry.

Ready-cut filters of various sizes should always be kept on hand. Filters are either cut by circular patterns of pasteboard or tin, or by *Mohr's* filter-pattern (Fig. 46), which consists of a quadrant made of tin plate, A, the straight sides of which have a rim turned up to the height of about a quarter of an inch; the papers, properly folded, with the edges at a right angle, are put into this, and a flat piece of tin-plate of the same form, B, is placed over them. The outer edge of the paper is then cut, with the scissors, to the pattern. Filters cut in this way are perfectly circular and of equal size.

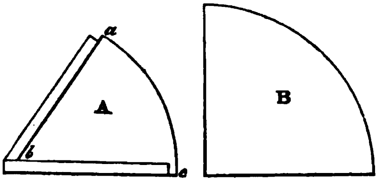

Fig. 46.

Several pairs of tin plates of various sizes (3, 4, 5, 6, 7, and 8 centimetre radius) should be procured for this purpose. The filter ought always to be sufficiently large to afford room for double the quantity of precipitate remaining on it after the filtration of the fluid.

The funnels used for filtration should be quite even, and not bulge at the sides; they should be inclined at the angle of 60°. Glass is the most suitable material for them.

The filter should never protrude beyond the funnel; the best way is to select filters the respective radii of which are one or two lines shorter than those of the funnels into which they are to be inserted.

The filter is firmly pressed into the funnel, to make the paper fit closely to the side of the latter; it is then moistened with water, which is allowed to pass through the neck, but must, on no account, be poured off by inverting the funnel.

The stands shown in Figs. 47 and 48 complete the apparatus for filtering.

The stand in Fig. 47 is more particularly adapted for the reception of larger funnels, and should therefore be made a little more solid than that in Fig. 48, which is intended for the reception of funnels of smaller size.

The stands are made of solid hard wood. The arm holding the funnel or funnels must slide easily up and down; but the screw, when tightened, must retain it firmly in position. The holes intended for the reception of the funnels, must be cut sloping conically downwards, to keep the funnels steadily in their place. The arm *b* (Fig. 47) serves for the reception of a washing-bottle.

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* *Plantamour* found the ash of Swedish filtering paper to consist of 63·23 silicic acid, 12·83 lime, 6·21 magnesia, 2·94 alumina, and 13·92 sesquioxide of iron, in 100 parts.

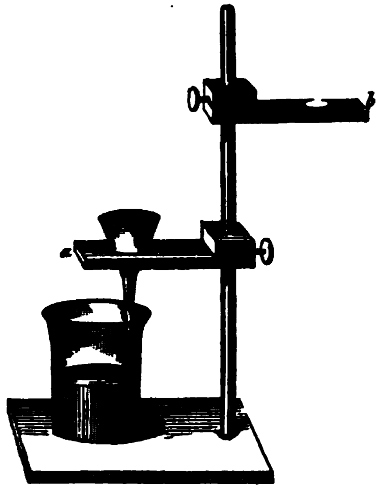

Fig. 47.

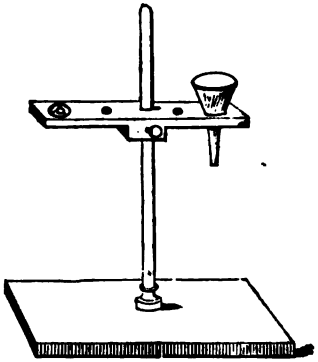

Fig. 48.

These stands are very convenient, and may be readily moved about without interfering with the operation.

§ 46.

bb. Rules to be observed in the Process of Filtration.

In the case of curdy, flocculent, gelatinous, or crystalline precipitates there is no great danger of any particles of the precipitate passing through the pores of the filter. But in cases where we have to deal with fine pulverulent precipitates, it is generally *necessary* and always *advisable*, to let the precipitate subside, and then filter the supernatant liquid, before proceeding to place the precipitate upon the filter. Substances which have been precipitated hot, are most properly filtered before cooling (provided always there be no objection to this course), since hot fluids run through the filter more speedily than cold ones. Some precipitates have a tendency to be carried through the pores of the filter along with the fluid; this may be prevented in some instances by modifying the latter. Thus sulphate of baryta, when filtered from an aqueous solution, passes rather easily through the filter—the addition of hydrochloric acid or chloride of ammonium prevents this in a great measure.

If the operator finds, during the filtration of a precipitate, that he has taken too small a filter to hold the precipitate conveniently, and so as to admit of its being properly washed, he had better use an additional filter, and thus distribute the precipitate over the two.

The fluid ought never to be poured directly upon the filter, but always down a glass rod, as shown in Fig. 45; and the lip or rim of the vessel from which the fluid is poured should always be slightly greased with tallow.* The stream ought invariably to be directed towards the sides of the filter, never to the centre, since this might occasion loss by splashing. In cases where the fluid has to be filtered off, with the least possible disturbance of the precipitate, the glass rod must not be placed, during the intervals, into the vessel containing the precipitate; but it may conveniently be put into a clean glass, which is finally rinsed with water upon the filter.

The filtrate is received either in flasks, or in beakers or dishes, according to the various purposes for which it may be intended. Strict care should be taken to guide the drops of fluid filtering through, down the side of the receiving vessel; they should never be allowed to fall into the centre of the filtrate, since this again might occasion loss by splashing. The best method is that shown in Fig. 47, viz., to rest the beak of the funnel against the upper part of the inside of the receiving vessel.

If the process of filtration is conducted in a place perfectly free from dust, there is no necessity to cover the funnel, nor the vessel receiving the filtrate; however, as this is but rarely the case, it is generally indispensable to cover both the funnel and the receiving vessel. This is best effected with round plates of sheet-glass; a small aperture for the tube of the funnel is cut out at the edge of the plates intended to cover the receiving vessel;—plates perforated in the centre are of no use for this purpose.

After the fluid and precipitate have been transferred to the filter, and the vessel which originally contained them has been washed repeatedly with water (which, of course, is also poured upon the filter), it happens generally that small particles of the precipitate remain adhering to the vessel, which cannot be removed with the glass rod. From beakers or dishes, these particles may be readily removed by means of a feather prepared for the purpose by tearing off nearly the whole of the plumules, leaving only a small piece at the end which should be cut perfectly straight. From flasks, minute portions of heavy precipitates which are not of an adhesive nature, are readily removed by blowing a jet of water into the flask, held inverted over the funnel; this is effected by means of the washing-bottle shown in Fig. 50, the outer end of the tube dipping in the water being turned upward instead of downward as in the engraving. If the minute adhering particles of a precipitate cannot be removed by mechanical means, solution in an appropriate menstruum must be resorted to, followed by re-precipitation. It is evident, therefore, that where we have to deal with substances for which we possess no solvent, such as sulphate of baryta, for instance, we must avoid precipitating in vessels from which the precipitate cannot be readily and completely removed by mechanical means.

§ 47.

cc. WASHING PRECIPITATES.

After having transferred the precipitate completely to the filter, we have next to perform the operation of washing; this is effected by means of a washing-bottle, such as Figs. 49—51 represent.

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* The tallow for this purpose may conveniently be kept in a small glass tube, corked at one end, and fitted with a piston, by means of which the tallow is pushed forward in proportion as it is required for use.

I prefer the one illustrated in Fig. 50. The handle serves to render its use more easy and convenient, more particularly in washing with hot water; it is made of wood, and fastened to the bottle with wire. If you wish to dispense with a handle to the washing-bottle, a sufficiently thick coil of string wound round the neck will answer the purpose almost equally well.

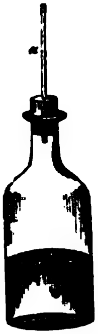

Fig. 49.

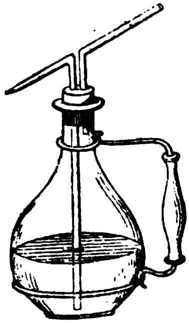

Fig. 50.

Care must always be taken to properly regulate the jet, as too impetuous a stream of water might occasion loss of substance.

In cases where a precipitate has to be washed with great care and caution, the apparatus illustrated in Fig. 51 will be found to answer very well.

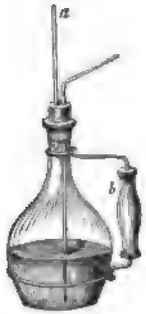

Fig. 51.

The construction of this apparatus does not require much explaining. The point *a* is drawn out at the end, and nipped off. When the flask is inverted, it supplies a fine continuous jet of water.

Precipitates requiring washing with water, are washed most expeditiously with hot water, provided always there be no special reason against its use. The washing-bottle shown in Fig. 50 is particularly well adapted for this purpose.

In cases where the washing of a precipitate has to be continued very long, we employ sometimes bottles of a peculiar construction, which saves the trouble of repeated application. Figs. 52 and 53 show washing-bottles of this description.

It will at once be clearly apparent from the engravings that the principle is the same in both. There is only this difference between them, that in 52 the two tubes are joined together in one piece, whilst in 53 they are separate. The construction of 52 is somewhat more difficult of illustration than that of 53. A brief exposition of the principle will clearly show this. Fig. 54 represents the cork with the tubes apart from the bottle. The arrangement is so contrived that no water can flow out of the bottle upon simple inversion; but it begins to flow immediately upon bringing the finger, or a small piece of paper, or some other substance, in contact with the water in the point *c*; the water will now run out in a continuous jet, whilst air passes into the bottle through the tube *a b*; the efflux of the water stops the moment the finger or piece of paper, &c., is removed from *c*.

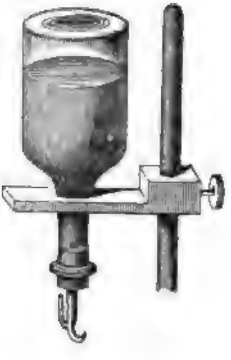

Fig. 52.

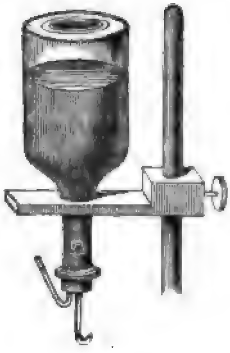

Fig. 53.

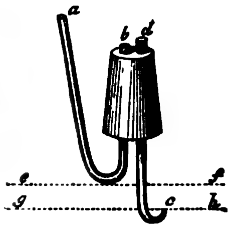

Fig. 54.

It is of great importance, for the proper construction and use of this washing apparatus, that the student should possess a clear and correct notion of the principle upon which its action depends. I will, therefore, here briefly explain this principle. In the first place, the non-efflux of water from *c* is owing to the circumstance that the pressure of the column of water occupying the space between the lines *e f* and *g h* is not *altogether*, but *nearly* sufficiently powerful to overcome the capillary attraction which the tube *a b* exercises upon the fluid;—in the second place, the efflux of water from *c* ensuing upon its being brought into contact with a body to which it may adhere, is owing to the pressure of the water column *f h*, assisted as it is now by the power of adhesion of the moistened body, overcoming the capillary attraction in *a b*. If the point *c* is put completely under water, the efflux will likewise cease, since this shortens the column *f h*. If the tube *d c* is lowered so as to place *c* below *g h*, the water will flow incessantly, the pressure of the increased column of water overcoming by itself the capillary attraction in *a b*. But if, on the contrary, *c d* is moved upwards, the pressure of the column *f h*, together with the force of adhesion of the substance in contact with it, will no longer be sufficiently powerful to overcome the capillary attraction in *a b*, and consequently no water will flow out. It will be readily conceived from the preceding remarks, that the construction of the tube in 52 offers some difficulties, since it is not by any means easy to fit *c* *exactly* at the required distance from the point where the tube *a b* is united to *c d*. In 53, on the other hand, the tube *c d* requires simply to be turned upward and downward until the desired point is attained. In the construction of the latter apparatus, care should be taken that the aperture *a* of *a b* be situated somewhat higher than *b*: if this precaution be neglected, water will be forced out with every bubble of air passing through the tube; moreover, *d* must abut somewhat higher than *b*, or, as soon as the surface of the water ceases to close *b*, the remainder will flow out in a continuous stream.

The process of washing by means of either of these bottles is easily performed. The bottle is placed inverted into the aperture contrived for its reception in the second arm of the filter-stand (see Fig. 47, *b*), and kept suspended above the funnel in such a manner that *c just* dips under the surface of the fluid. If the apparatus is well arranged, the water will now flow out of *c* in the same quantity as it runs off through the funnel.

To use, instead of these washing-bottles, narrow-necked flasks, inverted directly into the funnel, is quite inadmissible in cases where it is intended to determine the exact amount of the precipitated substance; since the ascending bubbles of air would invariably carry minute particles of the precipitate up into the flask.

Care should be taken, whilst washing the precipitate, no matter whether with or without a washing apparatus, to prevent the formation of channels in it, through which the water might flow without pervading the whole mass of the substance. If such channels have formed, the precipitate must be carefully stirred with a glass rod or a platinum spatula. As the use of washing-bottles tends to favor the formation of channels in precipitates in course of washing, it has of late been less employed, in the case of precipitates difficult to wash, the process described in § 48 being resorted to in preference.

The operation of washing may be considered completed when all soluble matter has been removed; whether this has been effected, may generally be ascertained by evaporating a drop of the last washings upon a platinum knife, and observing whether or not this leaves a residue. But in cases where the precipitate is not altogether insoluble in water (sulphate of strontia, for instance), recourse must be had to more special tests, which we shall have occasion to point out in the course of the work.

The operation of washing precipitates requires the greatest care and attention at the hands of the analytical chemist; it is self-evident that the imperfect washing of a precipitate must materially interfere with the accuracy of the results. The operation should, therefore, never be deemed concluded on a mere impression to that effect which the operator may be led to entertain; the information elicited by the application of the appropriate test or tests alone can safely be relied on.

§ 48.

SEPARATION OF PRECIPITATES BY DECANTATION AND FILTRATION COMBINED.

In the case of precipitates which, from their gelatinous nature, or from an admixture of certain salts that have been thrown down along with them, appear to oppose insuperable or, at all events, considerable obstacles to perfect washing on the filter, the following method is resorted to. Let the precipitate subside as far as practicable, pour the nearly clear supernatant liquid on the filter, stir the precipitate up with the washing fluid (in certain cases, where such a course is indicated, the mixture of the washing fluid with the precipitate may besides be heated to boiling), let it subside again, and repeat this operation until the precipitate is almost thoroughly washed. Transfer it now to the filter, and complete the operation with the washing-bottle (see § 47). This method ought to be resorted to more frequently than is usually the case; there are many precipitates that can be thoroughly washed only by its application.

In cases where it is not intended to weigh the precipitate washed by decantation, but to dissolve it again, the operation of washing is entirely completed by decantation, and the precipitate not even transferred to the filter. In such cases, the re-solution of the precipitate is effected in the vessel containing it, the filter being placed over the latter, and the solvent passed through it. Although the usual method applied to ascertain whether the operation of washing is actually completed, viz., testing a sample of the washings for one of the substances originally present in the solution from which the washed precipitate has been thrown down (for hydrochloric acid, for instance, with solution of nitrate of silver), will generally answer the purpose, there are cases in which it is not applicable. In such cases, and indeed in processes of washing by decantation generally, *Bunsen's* method is found the most convenient and practical; viz., to continue the process of washing until the fluid which had remained in the beaker, after the first decantation, has undergone a ten thousand-fold dilution. To effect this, measure with a slip of paper, applied, of course, outside the vessel, the height from the bottom of this beaker to the surface of the fluid remaining in it, together with the precipitate, after the first decantation; then fill the beaker with water, if possible, boiling, and measure the entire height of the fluid; divide the length of the second column by that of the first. Go through the same process each time you add fresh water, and always multiply the quotient found with the number obtained in the preceding calculation, until you reach 10,000.

§ 49.

FURTHER TREATMENT OF PRECIPITATES PREPARATORY TO THE PROCESS OF WEIGHING.

Before proceeding to weigh a precipitate, it is indispensable first to convert it into a form of accurately known composition. This is done either by drying the precipitate, or by heating it to redness. The former proceeding is more protracted and tedious in its application than the latter, and is, moreover, apt to give less accurate results. The process of drying is, therefore, as a general rule, applied only to precipitates which cannot bear exposure to a red heat without undergoing total or partial volatilization; or resorted to in cases where the residues left upon ignition have no uniform and constant composition; thus, for instance, drying is resorted to in the case of sulphide of mercury, sulphide of lead, and other metallic sulphides; and also in the case of cyanide of silver, potassio-bichloride of platinum, &c. &c.

But whenever the nature of the precipitated substance leaves the operator at liberty to choose between drying and heating to redness, the latter process is almost invariably preferred; thus precipitates of sulphate of baryta, sulphate of lead, and a great many other compounds, are heated to redness.

§ 50.

A. *Drying Precipitates.*

When a precipitate has been collected, washed, and dried on a filter, minute particles of it adhere so firmly to the paper that it is found impossible to remove them. The weighing of dried precipitates involves, therefore, in all accurate analyses, the drying and weighing of the filter also. Formerly, chemists used two filters of equal size, the one placed within the other; after the precipitate had been dried, the outer filter was taken off, and placed on the balance as a counterpoise to the inner filter which contained the precipitate. It was at the time assumed that filters of equal size were likewise of equal weight. This assumption, however, is inadmissible in minute and accurate analyses, since every experiment shows that even small filters, although of equal size, differ in weight to the extent of twenty, thirty, and even more milligrammes. To obtain accurate results, it is necessary to dry and weigh the filter before using it; the temperature at which the filter is dried must be the same as that to which it is intended subsequently to expose the precipitate. Another condition is that the filtering paper must not contain any substance liable to be dissolved by the fluid passing through it.

The process of drying filters (with precipitates) is conducted either in the water-bath or oil-bath, or in the air-bath according to the degree of heat required. The dried filter is always weighed in a vessel provided with a cover, mostly between two watch-glasses, pressed together with a clasp (§ 27), or in a platinum crucible. When the filter appears dry, it is placed between the warm watch-glasses, or in the warm crucible, allowed to cool under a bell-glass, over sulphuric acid, and weighed. The crucible or the watch-glasses, together with the filter, are then again exposed for some time to the required degree of heat, and, after cooling, weighed once more. If the weight does not differ from that found at first, the filter may be considered dry, and we have simply to note the collective weight of the watch-glasses, clasp, and filter, or of the crucible and filter.

After the washing of the precipitate has been concluded, and the water allowed to run off as far as practicable, the filter with the precipitate is taken off the funnel, folded up, and placed upon blotting-paper, which is then kept for some time in a moderately warm place, protected from dust; this serves to dry the precipitate in some measure, and thus facilitates the further process. The filter, with the precipitate, is now put into one of the watch-glasses, or into the uncovered platinum crucible, in which it was weighed previous to filtration, and is then exposed to the appropriate degree of heat, either in the water- or oil-bath, or in the air-bath, according to the nature of the precipitate. When it is judged that the precipitate is dry, the lid of the crucible is put on, or where a watch-glass has been used, the second watch-glass, with the clasp pushed over the two, and the crucible or the watch-glasses are then placed under a bell-glass, over sulphuric acid, where they are left to cool. After cooling they are weighed. The filter and the precipitate are then again exposed, in the same way, to the proper drying temperature, allowed to cool, and weighed again, the same process being repeated until the weight remains constant or differs only to the extent of a few deci-milligrammes. By subtracting from the weight found the tare of the crucible or watch-glasses and filter, we obtain the weight of the dry precipitate.

It happens sometimes that the precipitate nearly fills the filter, or retains a considerable amount of water; or sometimes the paper is so thin that its removal from the funnel cannot well be effected without tearing it. In all such cases, the best way is to let the filter and precipitate get nearly dry in the funnel, which may be effected readily by covering the latter with a piece of blotting-paper turned down over the rim, and placing it, supported on a broken beaker (Fig. 55), or some other vessel of the kind, on the steam-apparatus or sand-bath, or on a stove. In my laboratory the funnels are supported on cones, made of tin-plate, and open at both ends (Fig. 56). The larger cones are 12, the smaller 10 centimetres high; the lower diameter measures from 7 to 8, the upper from 4 to 6 centimetres.

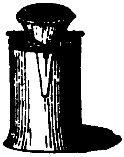

Fig. 55.

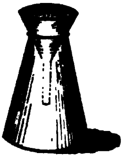

Fig. 56.

§ 51.

B. *Heating Precipitates to Redness.*

It was customary formerly, in this process, to dry the precipitate with the filter, then to scrape the latter clean and remove it, previously to heating the precipitate to redness. This proceeding was inevitably attended with the loss of the minute particles which, however so clean the filter may be scraped, will always adhere to it. Experience has shown that more accurate results are obtained if the filter is left with the precipitate, and the calculated weight of the ash of the paper subtracted from the weight of the precipitate after the process of ignition.

If care be taken to make the filters always of the same paper, and to cut every size by a pattern, the quantity of ash which each size yields upon incineration may be readily determined. It is necessary, however, to determine separately the quantity of ash left by ordinary filters, and that left by filters which have been washed with hydrochloric acid and water; as a general rule, the latter leave about half as much ash as the former. To determine the quantity of ash left by filters upon their incineration, take ten filters of the same size, burn them in an obliquely placed platinum crucible, or in a platinum dish, and continue the application of a red heat until every trace of carbon is consumed; then weigh the ash, and divide the amount found by 10; the quotient expresses, with sufficient precision, the average quantity of ash which every individual filter of the same size and of the same paper leaves upon incineration.

In the ignition of precipitates, the following four points have to be more particularly regarded:

1. No loss of substance must be incurred;
2. The ignited precipitates must really be the bodies they are represented to be in the calculation of the results;
3. The incineration of the filters must be complete;
4. The crucibles must not in any way be attacked by the process.

The following two methods of heating precipitates to redness seem to me the simplest and most appropriate of all that have as yet been proposed. The respective selection of either depends upon certain circumstances, which I shall immediately have occasion to point out. But no matter which method is resorted to, the precipitate must always be thoroughly dried, before it can properly be exposed to a red heat. The application of a red heat to moist precipitates, more particularly to such as are very light and loose in the dry state (silicic acid, for instance), involves always a risk of loss from the impetuously escaping aqueous vapors carrying away with them minute particles of the substance. Some other substances, as hydrate of alumina or hydrated sesquioxide of iron, for instance, have a tendency to concrete into small hard lumps: if such substances are not thoroughly dried previously to exposure to a red heat, they are liable, upon the application of that temperature, to fly about in the crucible with great violence. The best way of effecting the preliminary operation of drying, in such cases, is to expose the funnel bearing the filter with the precipitate, covered with a piece of blotting-paper turned over the rim, and supported in the manner shown in Figs. 55 and 56, to the heat of the sand-bath or water-bath, or of a stove, &c.

Respecting the *degree* of heat to be applied, and the *duration* of the process, these must, of course, depend upon the nature and properties of the precipitate and upon its deportment at a red heat. As a general rule, a moderate red heat, applied for about five minutes, is found sufficient to effect the purpose; the exceptions from the rule we shall have occasion to point out hereafter.

Whenever the choice is permitted between porcelain and platinum crucibles, the latter are always preferred, on account of their comparative lightness and superior solidity, and because they are more readily heated to redness. The crucible selected should always be of sufficient capacity, as the use of crucibles deficient in size involves the risk of loss of substance. The proper size, in most cases, is 4 centimetres in height, and 3·5 centimetres in diameter. That the crucible must be perfectly clean, both inside and outside, need hardly be mentioned. Dirt or impurities adhering to it may be removed by boiling with water, hydrochloric acid, or solution of soda. Where this fails to attain the desired end, a little bisulphate of potassa is fused in the crucible, the fluid mass shaken about inside, allowed to cool, and the crucible finally boiled with water. There are two ways of cleaning crucibles soiled outside; either the crucible is placed in a larger one, and the interstices between the two are filled with bisulphate of potassa, which is then heated to fusion; or the crucible is placed on a platinum wire triangle, heated to redness, and then sprinkled over with powdered bisulphate of potassa.

The ignition of precipitates is generally effected by means of a *Berzelius* spirit-lamp or a gas-lamp. When using *Bunsen's* gas-lamp for the purpose, the perforated porcelain plate belonging to it is put on the support (see Fig. 39).

When the crucible is clean, it is placed upon a clean platinum wire triangle, and heated to redness; it is then allowed to cool under the bell-glass, and afterwards weighed. This operation, though not indispensable, is still always advisable, to insure perfect correctness of the results, in so far as the weight of the crucible is concerned. The empty crucible may, indeed, also be weighed after the ignition of the precipitate; still it is always better to weigh it previously.

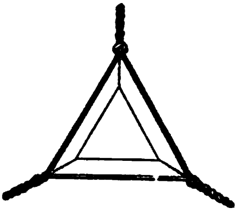
Fig. 57.

We will now proceed to the description of the two methods.

§ 52.

First Method. (*Heating the Precipitate to Redness, with simultaneous Incineration of the Filter.*)

This method is resorted to in cases where there is no danger of a reduction of the precipitate by the action of the carbon of the filter. The mode of proceeding is as follows:—

The perfectly dry filter, with the precipitate, is removed from the funnel, and its sides are gathered together at the top, so that the precipitate lies inclosed as in a small bag. The filter is now put into the crucible, which is then covered and exposed, over a spirit-lamp with double draught or over gas, to a moderate heat, to effect the slow charring of the filter; the cover is now removed, the crucible placed obliquely over the flame, and a stronger degree of heat applied, until complete incineration of the filter is effected; the lid, which had in the meantime best be kept on a porcelain plate, or in a porcelain crucible, is put on again, and a red heat applied for some time longer, if needed; the crucible is now allowed to cool a little, and is then, while still hot, though no longer red hot,* taken off with a pair of tongs of brass or polished iron (Figs. 58 and 59), and put under the bell-glass, where it is left to cool; it is finally weighed.

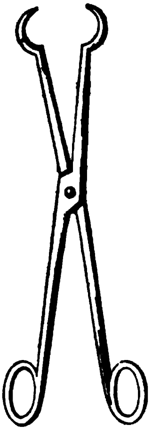

Fig. 58.

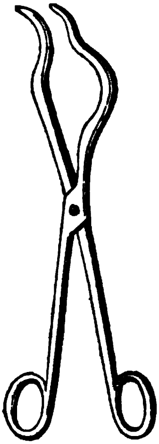

Fig. 59.

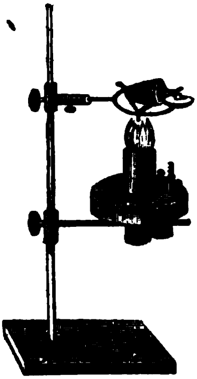

Fig. 60.

The combustion of the carbon of the filter may be promoted, in cases where it proceeds too slowly, by pushing the non-consumed particles, with a smooth and rather stout platinum wire, within the focus of the strongest action of the heat and air. Or the operator may also increase the draught of air, by leaning the lid of the crucible against the latter in the manner illustrated in Fig. 60.

It will occasionally happen that particles of the carbon of the filter obstinately resist incineration. In such cases the operation may be promoted by putting a small lump of fused, dry nitrate of ammonia into the crucible, placing on the lid and applying a gentle heat at first, which is gradually increased. However, as this way of proceeding is apt to involve some loss of substance, its application should not be made a general rule.

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* Taking hold of a *red-hot* platinum crucible with a pair of brass pincers, might cause the formation of black rings round it.

In cases where the precipitate is easily detached from the filter, the preceding method is occasionally modified in this, that the precipitate is put into the crucible, and the filter, with the still adhering particles, folded loosely together, and laid over the precipitate. In other respects, the operation is conducted in the manner above described.

§ 53.

SECOND METHOD. (*Heating the Precipitate to Redness, and incinerating the Filter separately.*)

This method is resorted to in cases where a reduction of the precipitate from the action of the carbon of the filter is apprehended; and also where the ignited precipitate is required for further investigation, in which the ash of the filter might form a disturbing element. It may be employed also, instead of the first method, in all cases where the precipitate is easily detached from the filter. The mode of proceeding is as follows:—

The crucible intended to receive the precipitate is placed upon a sheet of glazed paper; the perfectly dry filter with the precipitate is taken out of the funnel, and gently pressed together over the paper, to detach the precipitate from the filter; the precipitate is now placed in the crucible, and the particles still adhering to the filter are removed from it, as far as practicable, by gentle scraping and friction, and are then also transferred to the crucible. The filter is now spread open upon the sheet of glazed paper, and then folded in form of a little square box, enclosed on all sides by the parts turned up; any minute particles of the precipitate that may have dropt on the glazed paper are brushed into this little box, with the aid of a small feather; the box is closed again, rolled up, and one end of a sufficiently long platinum wire spirally wound round it. The platinum crucible with the precipitate being placed on or above a porcelain plate, the little scroll within the coil is lighted, and, during its combustion, held over the crucible in a position to make the falling particles of the precipitate or filter ash drop into it, or, at least, into the porcelain plate. In this way, and by occasionally holding the little scroll again in or near the flame, the incineration of the filter is readily and completely effected. When the operation is terminated, a slight tap will suffice to drop the ash and the remaining particles of the precipitate into the crucible, which is then covered, and the ignition completed as in § 52. Where it is intended to keep the ash separate from the precipitate, it is made to drop into the lid of the crucible, in which case it is better to ignite the crucible with the principal portion of the precipitate first. This method of incinerating the filter, devised by *Bunsen*, is preferable to the method formerly in use, in which the filter, freed, as far as practicable, from the precipitate, was burnt on the lid of the crucible, the operation being aided and promoted by gently pressing the still unconsumed particles with a smooth platinum wire, or platinum spatula, against the red-hot lid, to bring them into the most intimate contact with it. No matter which method of incineration is resorted to, the operation must always be conducted in a spot entirely protected from currents of air.

Certain precipitates suffer some essential modification in their properties, in their solubility, for instance, from the application of a red heat. In cases where a portion of a substance of the kind is required, after the weighing, for some other purpose with which the effects of a red heat would interfere, the two operations of drying and heating to redness may be combined in the following way:—The precipitate is collected on a filter dried at 212° F.; it is then also dried, at 212° F., and weighed. A portion of the dry precipitate is put into a tared crucible, and its exact weight ascertained; it is then exposed to a red heat, allowed to cool in the usual way, and weighed again; the diminution of weight which it has undergone is calculated on the whole amount of the precipitate.

§ 54.

5. ANALYSIS BY MEASURE (VOLUMETRICAL ANALYSIS).

The principle of volumetrical analysis has been explained already in the "Introduction," where we have seen how the quantity of protoxide of iron present in a fluid may be determined by means of a solution of permanganate of potassa of known strength. I will, however, adduce here a few more examples in illustration of this principle.

Suppose we have prepared a solution of chloride of sodium containing in 100 cubic centimetres 0·5846 grm. of the salt; with this solution we are enabled to precipitate exactly 1·0797 grm. of silver from a solution of that metal in nitric acid—the equivalent of chloride of sodium being 58·46, that of silver 107·97. Now, suppose we have an alloy before us, consisting of unknown quantities of silver and copper, and we want to determine the amount of silver contained in it: in this case, we need simply weigh off 1·0797 grm. of the alloy, dissolve carefully in nitric acid, and add to the solution our solution of chloride of sodium, drop by drop, until the whole of the silver is thrown down, and an additional drop fails to produce a further precipitate. The amount of silver present may now be calculated from the amount of solution of chloride of sodium used. Thus supposing we have used 80 cub. cent. of our solution, the amount of silver present in the alloy is = 80 per cent.; since, as 100 cub. cent. of the solution of chloride of sodium will throw down 1·0797 grm. of pure silver, it follows that every cub. cent. of the chloride of sodium solution corresponds to 1 per cent. of silver.

Another example. It is well known that iodine and sulphuretted hydrogen cannot exist together: whenever these two substances are brought in contact, decomposition immediately ensues, the hydrogen separating from the sulphur and combining with the iodine ($I + HS = HI + S$). Hydriodic acid exercises no action on starch paste, whereas the least trace of free iodine imparts to the latter substance a blue tint. Now, if we prepare an alcoholic solution containing in 100 cub. cent. 0·7463 grm. of iodine, we may with this decompose exactly 1 decigramme of sulphuretted hydrogen, for 17 : 126·88 : : 0·1 : 0·7463. Let us suppose, then, we have before us a fluid containing an unknown amount of sulphuretted hydrogen, which it is our intention to determine. We need simply add to it a little starch paste, and then, drop by drop, our solution of iodine, until a persistent blue coloration of the fluid indicates the formation of iodide of starch, and hence the absolute and complete decomposition of the sulphuretted hydrogen. The amount of the latter originally present in the fluid may now be readily calculated from the amount of solution of iodine used. Suppose, for instance, we have used 50 c. c. of iodine solution, the fluid contained originally 0·05 of sulphuretted hydrogen; since, as we have seen, 100 cub. cent. of our iodine solution will decompose exactly 0·1 grm. of that compound.

Solutions of accurately known composition, used for the purposes of volumetrical analysis, are called *standard solutions*. They may be prepared in two ways, viz., (*a*) by dissolving a weighed quantity of a reagent in a definite volume of fluid; or (*b*), by first preparing a suitably concentrated solution of the reagent required, and then determining its value or *standard*, *i.e.*, its exact strength by a series of experiments made with it upon weighed quantities of the body for the quantitative determination of which it is intended to be used.

In the preparation of standard solutions by method *a*, a certain definite standard is adopted once for all, which is usually based upon the principle of an exact correspondence between the number of grammes of the reagent contained in a litre of the fluid, and the equivalent number of the reagent ($H = 1$). In the case of standard solutions prepared by method *b*, this may also be easily done, by diluting to the required degree the still somewhat concentrated solution, after having accurately determined its strength; however, as a rule, this latter process is only resorted to in technical analyses, where it is desirable to avoid all calculation.

The determination of the standard solution intended to be used for volumetrical analysis is obviously a most important operation; since any error in this will, of course, necessarily falsify every analysis made with it. In scientific and accurate researches it is, therefore, always advisable, whenever practicable, to re-examine the standard solution, no matter whether prepared by method *a*, or by method *b*, with subsequent dilution to the required degree, by experimenting with it again upon accurately weighed quantities of the body for the quantitative determination of which it is intended to be used. If a standard solution keeps unaltered, this is a great advantage, as it dispenses the analyst from the necessity of determining its strength before every fresh analysis.

That particular change in the fluid operated upon by means of a standard solution which marks the completion of the intended decomposition, is termed the FINAL REACTION. This consists either in a *change of color*, as is the case when a solution of permanganate of potassa acts upon an acidified solution of protoxide of iron, or a solution of iodine upon a solution of sulphuretted hydrogen mixed with starch-paste; or in the *cessation of the formation of a precipitate* upon further addition of the standard solution, as is the case when a standard solution of chloride of sodium is used to precipitate silver from its solution in nitric acid; or in *incipient precipitation*, as is the case when a standard solution of silver is added to a solution of hydrocyanic acid mixed with an alkali; or in *a change in the action of the examined fluid upon a particular reagent*, as is the case when a solution of arsenite of soda is added, drop by drop, to a solution of chloride of lime, until the mixture no longer imparts a blue tint to paper moistened with iodide of potassium and starch-paste.

The more sensitive a final reaction is, and the more readily, positively, and rapidly it manifests itself, the better it is calculated to serve as the basis of a volumetrical method. In cases where it is an object of great importance to ascertain with the greatest practicable precision, the exact moment when the reaction is completed, the analyst should always, besides the actual standard solution, prepare another, ten times more dilute, and use the latter to finish the process, carried nearly to completion with the former.

But a good final reaction is not of itself sufficient to afford a safe basis for a good volumetrical method; this requires, as the first and most indispensable condition, that the particular decomposition which constitutes the leading point of the analytical process should—at least under certain known circumstances, remain unalterably the same. Wherever this is not the case—where the reaction varies with the greater or less degree of concentration of the standard fluid, or according as there may be a little more or less free acid present; or where it presents differences according to the greater or less rapidity of action of the standard solution; or where a precipitate formed in the course of the process has not the same composition throughout the operation—the basis of the volumetrical method is fallacious, and the method itself, therefore, of no value.

When the new system of volumetrical analysis first began to find favor with chemists, a great many volumetrical methods were proposed, based simply upon some final reaction, without a careful study of the ensuing decomposition; the result has been a superabundant crop of new volumetrical methods, of which a great many are totally fallacious and useless. In the special part of the present work I have taken care to separate the really good methods from the fallacious; the reader will there find that volumetrical analysis has not lately received the great accession of good methods which is generally supposed.

SECTION II.

REAGENTS.

§ 55.

For general information respecting reagents, I refer the student to my volume on "Qualitative Analysis."

The instructions given here will be confined to the preparation, testing, and most important uses of those chemical substances which subserve principally and more exclusively the purposes of quantitative analysis. Those reagents which are equally applied in qualitative investigations, have accordingly been treated of already in the volume on the qualitative branch of the analytical science, and will therefore be simply mentioned here by name.

The reagents used in quantitative analysis, are properly arranged under the following heads:—

A. Reagents for gravimetrical analysis in the humid way.
B. Reagents for gravimetrical analysis in the dry way.
C. Reagents for volumetrical analysis.
D. Reagents used in elementary organic analysis.

The mode of preparing fluids used in volumetrical analyses, and the absorption bulbs used in the analysis of gases, will be found where we shall have occasion to speak of their application.

A. REAGENTS FOR GRAVIMETRICAL ANALYSIS IN THE HUMID WAY.

I. SIMPLE SOLVENTS.

§ 56.

1. Distilled Water (see "Qual. Anal.").

Water intended for quantitative investigations must be perfectly pure. Water distilled from glass vessels leaves a residue upon evaporation in a platinum vessel (see experiment, No. 5), and is therefore inapplicable for many purposes; thus, for instance, we cannot use it to determine the exact degree of solubility of sparingly soluble substances. For certain uses it is necessary to free the water by ebullition from atmospheric air and carbonic acid.

2. Alcohol (see "Qual. Anal.").

a. Absolute alcohol. *b.* Rectified spirit of wine of various degrees of strength.

3. Ether.

The application of ether as a solvent is very limited. It is more frequently used mixed with spirit of wine, in order to diminish the solvent power of the latter for certain substances, *e. g.*, bichloride of platinum and chloride of ammonium. The ether employed in medicine will generally answer the purpose.

II. ACIDS AND HALOIDS.

a. Oxygen Acids.

§ 57.

1. Sulphuric Acid.

We require—
α. Concentrated sulphuric acid of the shops.
β. Concentrated pure sulphuric acid.
γ. Dilute sulphuric acid.

For the preparation, &c., of the three sorts, see "Qual. Anal."

2. Nitric Acid.

We require—
a. Pure nitric acid of 1·2 sp. gr. (see "Qual. Anal.").
b. Red fuming nitric acid (concentrated nitric acid containing some hyponitric acid).

Preparation.—Two parts of pure, dry nitrate of potassa are introduced into a capacious retort, and one part of concentrated sulphuric acid is poured upon this salt, either through the tubulature of the retort, or if a common non-tubulated one is used, through the neck by means of a long funnel-tube bent at the lower end, carefully avoiding soiling the neck of the retort. The latter being put into a vessel filled with sand, or, better still, with iron turnings, is then connected with a receiver, but not quite air-tight. The distillation is conducted at a gentle gradually-increased heat, and carried to dryness. The cooling of the receiver must be properly attended to during the distillation. In the preparation of small quantities, the retort is placed first on a piece of wire-gauze, and heated with charcoal; in this process it is always advisable to coat the retort by repeated application of a thin paste made of clay and water; a little borax or carbonate of soda should be added to the water used for the purpose.

Tests.—Red fuming nitric acid intended for analytical purposes must be in a state of the greatest possible concentration, and perfectly free from any admixture of sulphuric acid.

Uses.—This acid is a powerful dissolving and oxidizing agent; it serves more especially to convert sulphur and metallic sulphides into sulphuric acid and sulphates.

3. ACETIC ACID (see "Qual. Anal.").

4. TARTARIC ACID (see "Qual. Anal.").

b. Hydracids and Haloids.

§ 58.

1. HYDROCHLORIC ACID.

We require—

a. Pure hydrochloric acid of 1·12 sp. gr. (see "Qual. Anal.").

b. Pure fuming hydrochloric acid of about 1·18 sp. gr.

Preparation.—See "Qual. Anal." § 24, for the preparation of hydrochloric acid, with this modification, however, that only 3 or 4 parts of water, instead of 6, are put into the receiver, to 4 parts of chloride of sodium in the retort. The greatest care must be taken to keep the receiver cool, and to change it as soon as the tube through which the gas is conducted into it begins to get hot, since it is now no longer hydrochloric acid gas which passes over, but an aqueous solution of the gas, in form of vapor, which would simply weaken the fuming acid first passed over, if it were allowed to mix with it.

Tests.—Fuming hydrochloric acid, as well as the dilute acid, must be perfectly free from chlorine and sulphurous acid. For the mode of testing the acid for these impurities, see "Qual. Anal." § 24.

Uses.—Fuming hydrochloric acid has a much more energetic action than the dilute acid; it is, therefore, used instead of the latter in cases where a more rapid and energetic action is desirable.

2. CHLORINE and CHLORINE-WATER (see "Qual. Anal.").

3. NITRO-HYDROCHLORIC ACID (see "Qual. Anal.").

4. HYDROFLUOSILICIC ACID (see "Qual. Anal.").

c. Sulphur Acids.

1. HYDROSULPHURIC ACID (see "Qual. Anal.").

III. BASES AND METALS.

a. Oxygen Bases and Metals.

§ 59.

α. Alkalies.

1. Potassa and Soda (see "Qual. Anal.").

All the three sorts of the caustic alkalies mentioned in the qualitative part are required in quantitative analysis, viz., common solution of soda, hydrate of potassa purified with alcohol, and solution of potassa prepared with baryta. Pure solution of potassa may be obtained also by heating to redness for half an hour in a copper crucible, a mixture of 1 part of nitrate of potassa, and 2 or 3 parts of thin sheet copper cut into small pieces, treating the mass with water, allowing the oxide of copper to subside in a tall vessel, and removing the supernatant clear fluid by means of a syphon (*Wöhler*).

2. Ammonia (see "Qual. Anal.").

β. Alkaline Earths.

1. Baryta (see "Qual. Anal.").

The process recently proposed by *Fr. Mohr** for preparing crystals of baryta (precipitation of solution of nitrate of baryta with solution of soda), is altogether inapplicable for the preparation of baryta intended for analytical purposes, for instance, for the precipitation of magnesia in the separation of that earth from the alkalies, for the decomposition of silicates, &c.; since the almost unavoidable presence of soda in the baryta prepared in this way might lead to serious errors.

2. Lime.

Finely divided hydrate of lime mixed with water (milk of lime), is used more particularly to effect the separation of magnesia, &c., from the alkalies. Milk of lime intended to be used for that purpose must, therefore, be perfectly free from alkalies. To ensure this absolute purity of the reagent, the purest lime (calcined white marble) should be used, and the hydrate thoroughly washed, by repeated boiling with fresh quantities of distilled water. This operation is conducted best in a silver dish. When cold, the milk of lime so prepared is kept in a well-stoppered bottle.

γ. Heavy Metals, and their Oxides.

§ 60.

1. Zinc.

Zinc has of late been much used as a reagent in quantitative analysis. It serves more especially to effect the reduction of dissolved sesquioxide of iron to protoxide, and also the precipitation of copper from the solutions of that metal. Zinc intended to be used for the former purpose must be free from iron, for the latter free from lead, copper, and other metals which remain undissolved upon treating the zinc with dilute acids.

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* "Archiv der Pharm." 138, 33.

The distillation of zinc in the laboratory being a troublesome and costly operation, chemists generally use the raw product of the reduction of the ore by distillation, as this contains, at least in many cases, only such trifling traces of iron that it may be safely used for reducing solutions of sesquioxide of iron. The zinc of commerce, which is prepared by fusing the reduced metal in iron pots, contains much more iron, as melted zinc has the property of slowly dissolving that metal. Of the several sorts of unrefined zinc which I have had occasion to examine, Silesian zinc contains the least admixture of iron.

To procure zinc which leaves no residue upon solution in dilute sulphuric acid, it is indispensable to have recourse to re-distillation of the commercial article.

This is effected in a retort made of the material of Hessian or black-lead crucibles. The operation is conducted in a wind-furnace with good draught. The neck of the retort must hang down as perpendicular as possible. Under the neck is placed a basin or small tub, filled with water. The distillation begins as soon as the retort is at a bright red heat. As the neck of the retort is very liable to become choked up with zinc, or oxide of zinc, it is necessary to keep it constantly free by means of a piece of iron wire. The zinc obtained by this re-distillation is quite free from lead, or, at least, nearly so, but it still contains perceptible traces of iron (from the wire used to keep the neck of the retort free).

Tests.—The following is the simplest way of testing the purity of zinc: dissolve the metal in dilute sulphuric acid in a small flask provided with a gas-evolution tube, place the outer limb of the tube under water, and, when the solution is completed, let the water entirely or partly recede into the flask; after cooling, add to the fluid, drop by drop, a sufficiently dilute solution of permanganate of potassa. If a drop of that solution imparts the same red tint to the zinc solution, as to an equal volume of water, the zinc may be considered free from iron. I prefer this way of testing the purity of zinc to other methods, as it affords, at the same time, an approximate, or, if the zinc has been weighed, and the chameleon solution (which, in that case, must be considerably diluted) measured, an accurate and precise knowledge of the quantity of iron present. If lead or copper are present, these metals remain undissolved upon solution of the zinc.

2. Copper.

The copper of commerce, with the exception of the Japanese, which is not always easy to procure, is rarely sufficiently pure for analytical purposes. The following is the most convenient mode of preparing pure copper: precipitate the metal from a solution of the sulphate by a clean iron plate, free the precipitated copper from the iron by boiling with hydrochloric acid; wash, dry, fuse, and roll into thin sheets (*Fuchs*).

Tests.—Pure copper must dissolve completely in nitric acid, and addition of ammonia in excess to this solution must not, even after long standing, produce in it the faintest trace of a precipitate (iron, lead, &c.); neither should the addition of hydrochloric acid render the solution turbid (silver). Sulphuretted hydrogen must completely precipitate the copper from the solution.

Uses.—This metal serves us occasionally in *indirect* analysis; thus it is used, for instance, to determine the amount of copper present in a fluid, and also the amount of protoxide of iron existing in presence of the sesquioxide of that metal, &c. However, since the introduction of volumetrical methods, it is but rarely used in quantitative analysis.

3. Oxide of Lead.

Precipitate pure nitrate or acetate of lead with carbonate of ammonia, wash the precipitate, dry, and ignite gently to complete decomposition.

Oxide of lead is often used to fix an acid, so that it is not expelled even at a red heat.

4. Oxide of Mercury.

Preparation.—Pour a solution of chloride of mercury into a hot moderately dilute solution of soda, taking care to leave the solution of soda always in excess, and wash the yellow precipitate thoroughly by decantation.

Tests.—Oxide of mercury must leave no residue when heated to redness in a platinum crucible.

Uses.—This reagent serves, in quantitative investigations, principally to decompose chloride of magnesium in the process of separating magnesia from the alkalies.

b. Sulphur Bases.

1. Sulphide of Ammonium (see "Qual. Anal.").

We require both the colorless simple sulphide, and the higher yellow sulphide.

2. Sulphide of Sodium (see "Qual. Anal.").

IV. SALTS.

a. Salts of the Alkalies.

§ 61.

1. Sulphate of Potassa (see "Qual. Anal.").

2. Phosphate of Ammonia.

Preparation.—Mix pure dilute phosphoric acid (prepared from phosphorus) of 1·13 sp. gr. with an equal quantity of water, add pure ammonia to the mixture until it shows a strongly alkaline reaction, let it stand some time, filter, if necessary, and keep for use.

Tests.—Phosphate of ammonia must be free from any admixture of arsenic acid, nitric acid, and sulphuric acid, but more particularly of potassa, or soda. The presence of either of these alkalies may be detected by adding solution of pure acetate of lead, until the formation of a precipitate ceases, filtering, precipitating the excess of lead with sulphuretted hydrogen, filtering again, evaporating to dryness, and igniting the residue. If there now remains a residue soluble in water, and of alkaline reaction, this may be considered a conclusive proof of the presence of soda or potassa.

In most cases phosphate of soda (see "Qual. Anal.") may be substituted for phosphate of ammonia.

3. Oxalate of Ammonia (see "Qual. Anal.").

4. Acetate of Ammonia (see "Qual. Anal.").

5. Succinate of Ammonia.

Preparation.—Saturate succinic acid, which has been purified by recrystallization from its solution in nitric acid, with dilute ammonia. The reaction of the new compound should be rather slightly alkaline than acid.

Uses.—This reagent serves occasionally to separate sesquioxide of iron from other metallic oxides.

6. **Carbonate of Soda.**

This reagent is required both in solution and in pure crystals; in the latter form to neutralize an excess of acid in a fluid which it is desirable not to dilute overmuch.

7. **Carbonate of Ammonia** (see "Qual. Anal.").
8. **Bisulphite of Soda** (see "Qual. Anal.").
9. **Nitrite of Potassa** (see "Qual. Anal.").
10. **Bichromate of Potassa** (see "Qual. Anal.").
11. **Molybdate of Ammonia** (see "Qual. Anal.").
12. **Chloride of Ammonium** (see "Qual. Anal.").
13. **Cyanide of Potassium** (see "Qual. Anal.").

b. Salts of the Alkaline Earths.

§ 62.

1. **Chloride of Barium** (see "Qual. Anal.").

The following process, which I have of late devised, gives a very pure chloride of barium, free from lime and strontia:—Transmit through a concentrated solution of impure chloride of barium hydrochloric gas, as long as a precipitate continues to form. Nearly the whole of the chloride of barium present is by this means separated from the solution, in form of a crystalline powder. Collect this on a filter, let the adhering liquid drain off, wash the powder repeatedly with small quantities of pure hydrochloric acid, until a sample of the washings, diluted with water, and precipitated with sulphuric acid, gives a filtrate which, upon evaporation in a platinum dish, leaves no residue. The hydrochloric mother-liquor serves to dissolve fresh portions of witherite. I make use of the chloride of barium so obtained, principally for the preparation of perfectly pure carbonate of baryta, which is often required in quantitative analyses.

2. **Acetate of Baryta.**

Preparation.—Dissolve pure carbonate of baryta in moderately dilute acetic acid, filter, and evaporate the filtrate to crystallization.

Tests.—Dilute solution of acetate of baryta must not be troubled by solution of nitrate of silver. See also "Qual. Anal.," *Chloride of barium*, the same tests being also used to ascertain the purity of the acetate.

Uses.—Acetate of baryta is used instead of chloride of barium, to effect the precipitation of sulphuric acid, in cases where it is desirable to avoid the introduction of a metallic chloride into the solution, or to convert the base into an acetate. As the reagent is seldom required, it is best kept in crystals.

3. **Carbonate of Baryta** (see "Qual. Anal.").

4. **Chloride of Strontium.**

Preparation.—Chloride of strontium is prepared from strontianite or celestine, by the same process as chloride of barium from witherite. The pure crystals obtained are dissolved in spirit of wine of 96 per cent., the solution is filtered, and the filtrate kept for use.

Uses.—The alcoholic solution of chloride of strontium is used to effect the conversion of alkaline sulphates into metallic chlorides, in cases where it is desirable to avoid the introduction into the fluid of a salt insoluble in spirit of wine.

5. CHLORIDE OF CALCIUM (see "Qual. Anal.").

6. FLUORIDE OF CALCIUM.

This substance is used in quantitative analysis to displace and determine boracic acid; none but perfectly pure fluor-spar (like that of Derbyshire), free from any admixture of silicic acid, is applicable for this purpose. The hydrofluoric acid used in analytical investigations for the decomposition of silicates may be prepared from a less pure kind of fluor-spar.

Tests.—The best way of testing the purity of fluor-spar, in case of doubt, is to pulverize it finely, and to treat a weighed amount of the powder with pure concentrated sulphuric acid, in a platinum crucible, at a gentle heat, which is gradually increased to redness; the same operation being repeated until the weight of the residue remains constant. The fluor-spar may be considered pure if the calculated amount of sulphate of lime is obtained by this process.

7. SULPHATE OF MAGNESIA (see "Qual. Anal.").

This reagent is principally used to precipitate phosphoric acid from aqueous solutions. The solution required for this purpose should be kept ready prepared; it is made by dissolving 1 part of crystallized sulphate of magnesia and 1 part of pure chloride of ammonium in 8 parts of water and 4 parts of solution of ammonia, allowing the fluid to stand at rest for several days, and then filtering.

c. Salts of the Oxides of the Heavy Metals.

§ 63.

1. SULPHATE OF PROTOXIDE OF IRON (see "Qual. Anal.").

2. SESQUICHLORIDE OF IRON (see "Qual. Anal.").

3. ACETATE OF SESQUIOXIDE OF URANIUM.

Heat finely powdered pitchblende with dilute nitric acid, filter the fluid from the undissolved portion, and treat the filtrate with hydrosulphuric acid, to remove the lead, copper, and arsenic; filter again, evaporate the filtrate to dryness, extract the residue with water, and filter the solution from the oxides of iron, cobalt and manganese. Nitrate of sesquioxide of uranium crystallizes from the filtrate; purify this by recrystallization, and then heat the crystals until a small portion of the sesquioxide of uranium is reduced. Warm the yellowish-red mass thus obtained with acetic acid, filter and let the filtrate crystallize. The crystals are acetate of sesquioxide of uranium, and the mother-liquor contains the remainder of the nitrate (*Wertheim*).

Tests.—Solution of acetate of sesquioxide of uranium must not be altered by hydrosulphuric acid; carbonate of ammonia must produce in it a precipitate, soluble to a clear fluid in an excess of the precipitant.

Uses.—Acetate of sesquioxide of uranium may serve, in many cases, to effect the separation and quantitative determination of phosphoric acid.

4. **Nitrate of Silver** (see "Qual. Anal.").
5. **Acetate of Lead** (see "Qual. Anal.").
6. **Chloride of Mercury** (see "Qual. Anal.").
7. **Protochloride of Tin** (see "Qual. Anal.").
8. **Bichloride of Platinum** (see "Qual. Anal.").
9. **Sodio-Protochloride of Palladium** (see "Qual. Anal.").

B. REAGENTS FOR GRAVIMETRICAL ANALYSIS IN THE DRY WAY.

§ 64.

1. **Carbonate of Soda,** pure anhydrous (see "Qual. Anal.").
2. **Carbonate of Soda and Potassa** (see "Qual. Anal.").
3. **Hydrate of Baryta** (see "Qual. Anal." and § 59).
4. **Nitrate of Potassa** (see "Qual. Anal.").
5. **Nitrate of Soda** (see "Qual. Anal.").
6. **Borax** (fused).

Preparation.—Heat crystallized borax (see "Qual. Anal.") in a platinum or porcelain dish, until there is no further intumescence; reduce the porous mass to powder, and heat this in a platinum crucible until it is fused to a transparent mass. Pour the semi-fluid, viscid mass upon a fragment of porcelain. A better way is to fuse the borax in a net of platinum gauze, by making the gas blowpipe-flame act upon it. The drops are collected in a platinum dish. The vitrified borax obtained is kept in a well-stoppered bottle. But as it is always necessary to heat the vitrified borax previous to use, to make quite sure that it is perfectly anhydrous, the best way is to prepare it only when required.

Uses.—Vitrified borax is used to effect the expulsion of carbonic acid and other volatile acids, at a red heat.

7. **Bisulphate of Potassa.**

Preparation.—Mix 87 parts of neutral sulphate of potassa (see "Qual. Anal."), in a platinum crucible, with 49 parts of concentrated pure sulphuric acid, and heat to gentle redness, until the mass is in a state of uniform and limpid fusion. Pour the fused salt on a fragment of porcelain, or into a platinum dish standing in cold water. After cooling, break the mass into pieces, and keep for use.

Uses.—This reagent serves as a flux for certain native compounds of alumina and sesquioxide of chromium. Bisulphate of potassa is used also, as we have already had occasion to state, for the cleansing of platinum crucibles; for this latter purpose, however, the salt which is obtained in the preparation of nitric acid, will be found sufficiently pure.

8. **Carbonate of Ammonia** (solid).

Preparation. (See "Qual. Anal.")—This reagent serves to convert the bisulphates of the alkalies into neutral salts. It must completely volatilize when heated in a platinum dish.

9. **Nitrate of Ammonia.**

Preparation.—Neutralize pure carbonate of ammonia with pure nitric acid, warm, and add ammonia to slightly alkaline reaction; filter, if necessary, and let the filtrate crystallize. Fuse the crystals in a platinum dish, and pour the fused mass upon a piece of porcelain; break into pieces whilst still warm, and keep in a well-stoppered bottle.

Tests.—Nitrate of ammonia must leave no residue when ignited in a platinum dish.

Uses.—Nitrate of ammonia serves as an oxidizing agent; for instance, to convert lead into oxide of lead, or to effect the combustion of carbon in cases where it is desired to avoid the use of fixed salts.

10. CHLORIDE OF AMMONIUM.

Preparation and Tests.—See "Qual. Anal."

Uses.—Chloride of ammonium is often used to convert metallic oxides and acids, *e. g.*, oxide of lead, oxide of zinc, binoxide of tin, arsenic acid, antimonic acid, &c, into chlorides (ammonia and water escape in the process). Many metallic chlorides being volatile, and others volatilizing in presence of chloride of ammonium fumes, they may be completely removed by igniting them with chloride of ammonium in excess, and thus many compounds, *e. g.*, alkaline antimonates, may be easily and expeditiously analysed. Chloride of ammonium is also used to convert various salts with other acids into chlorides, *e.g.*, small quantities of alkaline sulphates.

11. HYDROGEN GAS.

Preparation.—Hydrogen gas is evolved when dilute sulphuric acid is added to granulated zinc. It may be procured absolutely pure by transmitting it, in the first place, through a long glass tube loosely filled with cotton, saturated with solution of chloride of mercury; afterwards, through a solution of potassa; and, finally, through concentrated sulphuric acid. In most cases, however, it is only necessary to dry it, by transmission through sulphuric acid, or through a tube filled with chloride of calcium.

Tests.—Pure hydrogen gas is inodorous. It ought to burn with a colorless flame, which, when cooled by depressing a porcelain dish upon it, must deposit nothing on the surface of the dish except pure water (free from acid reaction).

Uses.—Hydrogen gas is frequently used, in quantitative analysis, to reduce oxides, chlorides, sulphides, &c., to the metallic state.

12. CHLORINE.

Preparation. (See "Qual. Anal.")—Chlorine gas is purified and dried by transmitting it, first, through a washing-bottle containing concentrated sulphuric acid, and, finally, through a tube filled with chloride of calcium; the latter may, however, be omitted.

Uses.—Chlorine gas serves principally to produce chlorides, and to separate the volatile from the non-volatile chlorides; it is also used to displace and indirectly determine bromine and iodine.

C. REAGENTS USED IN VOLUMETRICAL ANALYSIS.

§ 65.

Under this head are arranged here the most important of those substances, which serve for the preparation and testing of the fluids required in volumetrical analysis, and have not been given *sub A* and *B*.

1. Pure crystallized Oxalic Acid.

The introduction of crystallized oxalic acid as a volumetrical agent in alkalimetry and acidimetry is due to *Fr. Mohr.* It is also employed to determine the strength or *standard*, of a solution of permanganate of potassa, 1 equivalent of permanganic acid being required to convert 5 equivalents of oxalic acid into carbonic acid ($Mn\ 2\ O_7 + 2\ S\ O_3 + 5\ C_2\ O_3 = 2\ Mn\ O,\ S\ O_3 + 10\ C\ O_2$). We use in all cases the pure crystallized acid which has the formula $C_2\ O_3\ H\ O + 2$ aq., and of which the equivalent is accordingly 63.

Preparation.—Pour over powdered oxalic acid of commerce, in a flask, lukewarm distilled water, in such proportion as will leave a large amount of the acid undissolved (*Fr. Mohr*). Filter, crystallize, and let the crystals drain; then spread them out on blotting-paper, and let them get thoroughly dry, at the common temperature, in a place free from dust; or press them gently between sheets of blotting-paper, and repeat the operation with fresh sheets, until the crystals are quite dry.

Tests.—The crystals of oxalic acid must not show the least sign of efflorescence; they must dissolve in water to a perfectly clear fluid; when heated on platinum, they must leave no fixed and incombustible residue (carbonate of lime, carbonate of potassa, &c.). If the acid obtained by a first crystallization fails to satisfy these requirements, it must be recrystallized.

2. Tincture of Litmus.

Preparation.—Digest 1 part of litmus of commerce with 6 parts of water, on the water-bath, for some time, filter, divide the blue fluid into 2 portions, and saturate, in one half, the free alkali, by stirring repeatedly with a glass rod dipped in very dilute nitric acid, until the color just appears red; add the remaining blue half, together with 1 part of strong spirit of wine, and keep the tincture, which is now ready for use, in a small open bottle, not quite full, in a place protected from dust. In a stoppered bottle the tincture would speedily lose color.

Tests.—Litmus tincture is tested by coloring with it about 100 cubic centimetres of water distinctly blue, dividing the fluid into two portions, and adding to the one the least quantity of a dilute acid, to the other a trace of solution of soda. If one portion acquires a distinct red, the other a distinct blue tint, the litmus tincture is fit for use, as neither acid nor alkali predominates.

3. Permanganate of Potassa.

Preparation.—Mix 8 parts of very finely powdered pure pyrolusite, or binoxide of manganese, with 7 parts of chlorate of potassa, put the mixture into a shallow cast-iron pot, and add a highly concentrated solution of 10 parts of hydrate of potassa ($K\ O,\ H\ O$), or 37 parts of a solution of potassa of 1·27 specific gravity (the same solution as is used in elementary organic analysis); evaporate to dryness, stirring the mixture during the operation; put the residue before it has absorbed moisture, into an iron or Hessian crucible, and expose to a dull-red heat, with frequent stirring with an iron rod or iron spatula, until no more aqueous vapors escape, and the mass is in a faint glow. Remove the crucible now from the fire, and transfer the friable mass to an iron pot. If you have hydrate of potassa in the solid state, fuse it together with the chlorate of potassa, and then add the powdered binoxide of manganese. Reduce the friable mass to coarse powder, and transfer this, in small portions at a time, to a porcelain basin containing 400 parts of water heated to ebullition; keep boiling, replacing the evaporating water, until the green color of the manganate of potassa has changed to the violet-red tint of the permanganate, which change is attended with separation of hydrated binoxide of manganese. Should the presence of a considerable excess of potassa impede and delay the manifestation of this change, notwithstanding that proper care has been taken to make the solution sufficiently dilute, the desired conversion of the manganate to permanganate may be effected immediately by cautiously neutralizing part of the excess of potassa with nitric acid.

Let the solid particles now subside, decant the fluid into a suitable vessel, wash the deposit repeatedly by decantation, add the washings to the solution, mix, let the few solid particles still suspended in the fluid thoroughly subside, and finally decant the clear fluid from the trifling deposit into the bottle in which it is to be kept.

4. AMMONIO-SULPHATE OF PROTOXIDE OF IRON.

$$(\mathrm{Fe\,O,\,S\,O_3 + N\,H_4\,O,\,S\,O_3 + 6\,aq.})$$

Fr. Mohr has proposed to employ this double salt, which is not liable to efflorescence and oxidation, as an agent to determine the strength or standard, of the chameleon solution.

Preparation.—Take two equal portions of dilute sulphuric acid, and warm the one with a moderate excess of small iron nails free from rust, until the evolution of hydrogen gas has altogether or very nearly ceased; neutralize the other portion exactly with carbonate of ammonia, and then add to it a few drops of dilute sulphuric acid. Filter the solution of the sulphate of the protoxide of iron to that of the sulphate of ammonia, evaporate the mixture a little, if necessary, and then allow the salt to crystallize. Let the crystals, which are hard and of a pale green color, drain on a funnel, then wash them with a little water, dry thoroughly on blotting-paper, in the air, and keep for use.

The equivalent of the salt (196) is exactly 7 times that of iron (28).

5. PURE IODINE.

Preparation.—Triturate iodine of commerce with $\frac{1}{8}$th part of its weight of iodide of potassium, dry the mass in a large watch-glass with ground rim, warm this gently on a sand-bath, or on an iron plate, and as soon as violet fumes begin to escape, cover it with another watch-glass of the same size. Continue the application of heat until all the iodine is sublimed, and keep in a well-closed glass bottle. The chlorine or bromine, which is often found in iodine of commerce, combines, in this process, with the potassium, and remains in the lower watch-glass, together with the excess of iodide of potassium.

Tests.—Iodine purified by the process just now described, must leave no fixed residue when heated on a watch-glass. But, even supposing it should leave a trace on the glass, it would be of no great consequence, as the portion of iodine intended for use has to pass once more through a process of sublimation.

Uses.—Pure iodine is used to determine the amount of iodine contained in the solution of iodine in iodide of potassium, employed in many volumetrical processes.

6. Iodide of Potassium.

Small quantities of this article may be procured cheaper in commerce than prepared in the laboratory. For the preparation of iodide of potassium intended for analytical purposes I recommend *Baup's* method, improved by *Frederking*, because the product obtained by this process is free from iodic acid.

Tests.—Put a sample of the salt in dilute sulphuric acid. If the iodide is pure, it will dissolve without coloring the fluid; but if it contain iodate of potassa, the fluid will acquire a brown tint, from the action of free iodine ($K\,I + H\,O + S\,O_3 = K\,O,\,S\,O_3 + H\,I$ and $I\,O_5$ and $5\,H\,I = 5\,H\,O$ and $6\,I$, which remain in solution in the hydriodic acid). Mix the solution of another sample with nitrate of silver, so long as a precipitate continues to form; add solution of ammonia in excess, shake the mixture, filter, and supersaturate the filtrate with nitric acid. The formation of a white, curdy precipitate indicates the presence of chloride in the iodide of potassium. Presence of sulphate of potassa is detected by means of solution of chloride of barium, with addition of some hydrochloric acid.

Uses.—Iodide of potassium is used as a solvent for iodine, in the preparation of standard solutions of iodine; it is employed also to absorb free chlorine. In the latter case every equivalent of chlorine liberates an equivalent of iodine, which is retained in solution by the agency of the excess of iodide of potassium. The iodide of potassium intended for these uses must be free from iodate and carbonate of potassa; the presence of trifling traces of chloride of potassium or sulphate of potassa is of no consequence.

7. Sulphurous Acid.

Preparation.—Conduct the sulphurous acid gas disengaged from copper turnings and concentrated sulphuric acid, and washed (see "Qualitative Analysis," fifth edition, § 46), into water to saturation, and keep the solution in several well-stoppered bottles.

This concentrated solution serves to prepare the highly dilute solution of sulphurous acid used in *Bunsen's* method of determining iodine.

8. Arsenious Acid.

The arsenious acid sold in the shops in large pieces, externally opaque, but often still vitreous within, is generally quite pure. The purity of the article is tested by moderately heating it in a glass tube, open at both ends, through which a feeble current of air is transmitted. Pure arsenious acid must completely volatilize in this process; no residue must be left in the tube upon the expulsion of the sublimate from it. If a non-volatile residue is left which, when heated in a current of hydrogen gas, turns black, the arsenious acid contains teroxide of antimony, and is unfit for use in analytical processes. Arsenious acid is employed, in form of arsenite of soda, to determine hypochlorous acid, free chlorine, iodine, &c.

9. Chloride of Sodium.

Perfectly pure rock-salt is best suited for analytical purposes. It must dissolve in water to a clear fluid; oxalate of ammonia, phosphate of soda, and chloride of barium must not trouble the solution. Pure chloride of sodium may be prepared also by the following process: conduct into a concentrated solution of chloride of sodium hydrochloric gas to saturation, collect the small crystals of chloride of sodium which separate on a funnel, let them thoroughly drain, wash with hydrochloric acid, and dry the chloride of sodium finally in a porcelain dish, until the hydrochloric acid adhering to it has completely evaporated. The mother-liquor, which contains the small quantities of sulphate of lime, chloride of magnesium, &c., originally present in the chloride of sodium, is, at the next preparation of hydrochloric acid ("Qualitative Analysis," fifth English edition, § 24), added to the ingredients in the retort, instead of a corresponding portion of water.

Uses.—Chloride of sodium serves as a volumetrical precipitating agent in the determination of silver, and also to determine the strength or standard of solutions of silver intended for the estimation of chlorine.

10. Metallic Silver.

The silver obtained by the proper reduction of the pure chloride of the metal alone can be called chemically pure. The standard silver of the refiner, precipitated by copper, is never absolutely pure, but contains generally about $\frac{1}{1000}$th of copper. However, the most convenient way for chemists is to use the silver-leaf sold by refiners as chemically pure silver.

Chemically pure silver is only used in small quantity to prepare the dilute solution employed for the quantitative determination of silver. The solution of silver required for the estimation of chlorine may be made with the standard silver of the Mint, as the strength of this solution had always best be determined *after* the preparation, by means of pure chloride of sodium.

D. REAGENTS USED IN ELEMENTARY ORGANIC ANALYSIS.

§ 66.

1. Oxide of Copper.

Preparation.—Stir pure copper scales with pure nitric acid in a porcelain dish to a thick paste; after the effervescence has ceased, heat gently on the sand-bath until the mass is perfectly dry. Transfer the green basic salt produced to a Hessian crucible, and heat to moderate redness, until no more fumes of hyponitric acid escape, which may be readily ascertained by introducing a small portion of the mass into a test tube, closing the latter with the finger, heating to redness, and then looking through the tube lengthways; in most instances, however, the smell will sufficiently indicate whether the evolution of nitrous vapors has ceased. The uniform decomposition of the salt in the crucible may be promoted by stirring the mass from time to time with a hot glass rod. When the crucible has cooled a little, reduce the mass, which now consists of pure oxide of copper, to a tolerably fine powder, by triturating it in a brass or porcelain mortar; pass the powder through a metal sieve, and keep the sifted portion in a well-stoppered bottle for use. It is always advisable to leave a small portion of the oxide in the crucible, and to expose this again to an intense red heat. This Agglutinated portion is not pounded, but simply broken into small fragments, which are kept in a separate bottle.

Tests.—Pure oxide of copper is a compact, heavy, deep-black powder, gritty to the touch, and absolutely insoluble in water; upon exposure to a red heat, it must evolve no hyponitric acid fumes, nor carbonic acid; the latter would indicate presence of fragments of charcoal, or particles of dust. That portion of the oxide which has been exposed to an intense red heat should be hard, and of a grayish-black color.

Uses.—Oxide of copper serves to oxidize the carbon and hydrogen of organic substances, yielding up its oxygen wholly or in part, according to circumstances. That portion of the oxide which has been heated to the most intense redness is particularly useful in the analysis of volatile fluids.

N.B. The reduced copper or suboxide may be again oxidized with nitric acid, and may thus be used repeatedly for the same purpose. Should it have become mixed with alkaline salts in the course of the analytical process, it may be freed from such admixture by digesting with very dilute cold nitric acid, and washing afterwards with water.

2. Chromate of Lead.

Preparation.—Precipitate a clear filtered solution of acetate of lead, slightly acidulated with acetic acid, with a small excess of bichromate of potassa: wash the precipitate thoroughly by decantation, and finally on a linen strainer; dry the washed precipitate, put it into a Hessian crucible, and heat to bright redness until the mass is fairly in fusion. Pour the fused mass upon a stone slab or iron plate, break, pulverize, pass through a fine metallic sieve, and keep the tolerably fine sifted powder for use.

Tests.—Chromate of lead is a heavy powder, of a dirty yellowish-brown color; it is insoluble in water. It must evolve no carbonic acid upon the application of a red heat; the evolution of carbonic acid would indicate contamination with organic matter, dust, &c.

Uses.—Chromate of lead serves, the same as oxide of copper, for the combustion of organic substances. It is converted, in the process of combustion, into sesquioxide of chromium and basic chromate of lead. It suffers the same decomposition, with evolution of oxygen, when heated by itself above its point of fusion. The property of chromate of lead to fuse at a red heat renders it preferable to oxide of copper as an oxidizing agent, in cases where we have to act upon difficulty combustible substances.

N.B. Chromate of lead may be used a second time. For this purpose it is fused again, and the mass reduced to powder, in the same way as stated before. Should it be deemed necessary, the second fusion may be preceded by washing.

3. Chlorate of Potassa.

Preparation.—Heat commercial chlorate of potassa in a platinum or porcelain dish, until the mass is fairly in fusion; but no longer; pour the fused mass into a platinum dish, and break it, whilst still hot, into small pieces. Preserve in a well-stoppered bottle for use.

Uses.—Chlorate of potassa yields up all its oxygen at a high temperature; it is used, accordingly, to effect the complete oxidation of difficulty combustible organic substances. The way of applying it will be found described in the chapter on elementary organic analysis.

4. OXYGEN GAS.

Preparation.—Triturate 100 grammes of chlorate of potassa with exactly 0·1 grm. of finely powdered sesquioxide of iron, and introduce the mixture into a plain retort, which must not be more than half full; expose the retort, over a charcoal fire, to a gentle, gradually increased heat. As soon as the salt begins to fuse, shake the retort a little, that the contents may be uniformly heated. The evolution of oxygen speedily commences, and proceeds rapidly, but not impetuously, provided always, of course, the above proportion between the chlorate of potassa and the sesquioxide of iron be strictly adhered to. As soon as the air is expelled from the retort, connect the glass tube, fixed in the neck of the retort by means of a tight-fitting perforated cork, with an india-rubber tube inserted into the lower orifice of the gasometer; the glass tube must be sufficiently wide, and there must be sufficient space left around the india-rubber to permit the free efflux of the displaced water. Continue the application of heat to the retort until the evolution of gas has altogether, or very nearly ceased, even when carried to incipient redness. It is advisable to coat the retort up to the middle of the body with several layers of a thin paste made of clay and water, with addition of a little carbonate of soda or borax.

100 grammes of chlorate of potassa give about 27 litres of oxygen gas.

The oxygen gas produced by this process is moist, and may contain traces of carbonic acid gas, and also of chlorine. The gas prepared from a mixture of chlorate of potassa with a comparatively large proportion of binoxide of manganese always contains a rather considerable quantity of chlorine gas. These impurities must be removed, and the oxygen gas thoroughly dried, before it can be used in elementary organic analysis. The gas is, therefore, passed from the gasometer, first through a *Liebig's* bulb-apparatus filled with solution of potassa of 1·27 sp. gr., then through a U-tube containing pumice-stone, moistened with sulphuric acid, afterwards through several tubes filled with hydrate of potassa, and lastly through a tube containing chloride of calcium.

Tests.—A chip of wood which has been kindled and blown out, so as to leave a spark at the extremity, must immediately burst into flame in a current of oxygen gas. The gas must not trouble lime-water, nor solution of nitrate of silver when transmitted through these fluids.

5. SODA-LIME (mixture of caustic lime and hydrate of soda).

Preparation.—Dissolve commercial crystallized carbonate of soda, in the manner described in the "Qualitative Analysis;" ascertain the specific gravity of the solution, then add a weighed amount of the best caustic lime, in the exact proportion of two parts of anhydrous caustic lime to one part of hydrate of soda contained in the solution, and evaporate to dryness in an iron vessel. Heat the residue in an iron or Hessian crucible, keep for some time at a moderate red heat, and reduce the mass, whilst still warm, to a tolerably fine powder, by pounding and sifting through a metallic sieve. Keep the powder in a well-stoppered bottle.

Tests.—Soda-lime must but slightly effervesce when treated with hydrochloric acid in excess; but more particularly, it must not evolve ammonia, when mixed with pure sugar, and heated to redness.

Uses.—Soda-lime serves in the analysis of nitrogenous organic substances. For the *rationale* of its action, see the chapter on Elementary Organic Analysis.

6. BICARBONATE OF SODA.

In one of the processes of elementary organic analysis of nitrogenous substances, bicarbonâte of soda serves to evolve the carbonic acid by means of which the atmospheric air is expelled from the combustion tube. The commercial bicarbonate is sufficiently pure for this purpose; but it must be perfectly dry.

7. METALLIC COPPER.

Metallic copper serves, in the analysis of nitrogenous substances, to effect the reduction of the nitric oxide gas that may form in the course of the analytical process.

It is used either in the form of turnings, or in that of close wire spirals; or of small rolls made of thin sheet copper. A length of from 7 to 10 centimetres is given to the spirals or rolls, and just sufficient thickness to admit of their being inserted into the combustion tube. To have it perfectly free from dust, oxide, &c., it is first heated to redness in the open air, in a crucible, until the surface is oxidized; it is then put into a glass or porcelain tube, through which an uninterrupted current of dry hydrogen gas is transmitted; finally, when all atmospheric air has been expelled from the evolution apparatus and the tube, the latter is in its whole length heated to redness. The operator should make sure that the atmospheric air has been thoroughly expelled, before he proceeds to apply heat to the tube: neglect of this precaution may lead to an explosion.

8. POTASSA.

a. Solution of Potassa.

Solution of potassa is prepared from purified potassa, with the aid of milk of lime, in the way described in the "Qualitative Analysis" for the preparation of solution of soda. The proportions are—1 part of potassa to 12 parts of water, and two-third parts of lime made into paste with three times the quantity of warm water.

The decanted clear solution is evaporated, in an iron vessel, over a strong fire, until it has a specific weight of 1·27; it is then, whilst still warm, poured into a bottle, which is well-closed, and allowed to stand at rest until all solid particles have subsided. The clear solution is finally drawn off from the deposit, and kept for use.

b. Hydrate of Potassa (common).

The commercial hydrate of potassa in sticks will answer the purpose. If you wish to prepare it, evaporate solution of potassa (*a*) in a silver vessel, over a strong fire, until the residuary hydrate flows like oil, and white fumes begin to rise from the surface. Pour the fused mass out on a clean iron plate, and break it up into small pieces. Keep in a well-stoppered bottle for use.

c. Hydrate of Potassa (purified with alcohol), see "Qual. Anal." 5th edition, § 30, *b*.

Uses.—Solution of potassa serves for the absorption, and accordingly for the quantitative estimation of carbonic acid. In many cases, a tube filled with hydrate of potassa is used, in addition to the apparatus filled with solution of potassa. Hydrate of potassa purified with alcohol, and perfectly free from sulphate of potassa, is employed for the determination of sulphur in organic substances.

9. CHLORIDE OF CALCIUM.

a. Crude fused Chloride of Calcium.

Preparation.—Digest, with warm water, the residuary mixture of chloride of calcium and lime which remains after the preparation of ammonia; filter, neutralize the alkaline filtrate exactly with hydrochloric acid, and evaporate to dryness in an iron pan; fuse the residue in a Hessian crucible, pour out the fused mass, and break into pieces. Preserve it in well-stoppered bottles.

b. Pure Chloride of Calcium.

Preparation.—Dissolve the crude chloride of calcium of *a* in lime-water, filter the solution, and neutralize with a few drops of hydrochloric acid; evaporate, in a porcelain dish, to dryness, and expose the residue for several hours to a tolerably strong heat (about 392° F.), on the sand-bath. The white and porous mass obtained by this process consists of $Ca\,Cl + 2\,aq$.

Uses.—The crude fused chloride of calcium serves to dry moist gases; the pure chloride is used in elementary organic analysis for the absorption and estimation of the water formed by the hydrogen contained in the analysed substance. The solution of the pure chloride of calcium must not show an alkaline reaction.

10. BICHROMATE OF POTASSA.

Bichromate of potassa of commerce is purified by repeated recrystallization, until chloride of barium produces in the solution of a sample of it in water, a precipitate which completely dissolves in hydrochloric acid. Bichromate of potassa thus perfectly freed from sulphuric acid, by repeated recrystallization, is required more particularly for the oxidation of organic substances with a view to the quantitative estimation of the sulphur contained in them. Where the salt is intended for other purposes, *e.g.*, to determine the carbon of organic bodies, by heating them with chromate of potassa and sulphuric acid, one recrystallization is sufficient.

SECTION III.

FORMS AND COMBINATIONS IN WHICH SUBSTANCES ARE SEPARATED FROM EACH OTHER, OR IN WHICH THEIR WEIGHT IS DETERMINED.

§ 67.

THE quantitative analysis of a compound substance requires, as the first and most indispensable condition, a correct and accurate knowledge of the composition and properties of the new combinations, into which it is intended to convert its several individual constituents, for the purpose of separating them from one another, and determining their respective weight. Regarding the properties and deportment of the new compounds, we have to inquire more particularly, in the first place, how they behave with solvents; secondly, what is their deportment in the air; and, thirdly, what phenomena they manifest when exposed to the action of a red heat? It may be laid down as a general rule that compounds are the better adapted for quantitative determination the more insoluble they are, and the less alteration they undergo upon exposure to air or to a high temperature.

The composition of bodies is expressed either in percentage proportions, or in stœchiometrical or symbolic formulæ; by means of the latter, the constitution of the more frequently recurring compounds may be more easily committed to memory. In this section the composition of the substances treated of is given in four different ways, in as many columns: the first column gives the composition of the substance in symbols; the second, in equivalents (O = 100); the third, in equivalents (H = 1); the fourth, in percentage proportions. With respect to its composition, a compound is the better adapted for quantitative determination the less it contains relatively of the substance which it is intended to determine; since the less the relative proportion of the latter, the less influence will any error or loss of substance that may occur in the course of the analytical process exercise upon the accuracy of the results. Thus, ammonio-bichloride of platinum, for instance, is, in this respect, better adapted for the determination of nitrogen than chloride of ammonium; since 100 parts of the double chloride contain only 6·27 of that element, whilst 100 parts of the latter contain 26·2 of it.

Suppose we have to analyse a nitrogenous substance;—we estimate its nitrogen in the form of bichloride of platinum and chloride of ammonium. When the process is conducted with absolute accuracy, 0·300 grm. of the analysed body yields 1·000 grm. of ammonio-bichloride of platinum: 100 parts of this double chloride contain 6·27 parts of nitrogen, 1·000 contains therefore 0·0627 of that element. These 0·0627 have been derived from 0·300 of substance; 100 parts of the analysed body, consequently, contain 20·90 of nitrogen.

We now make a second analysis, in which we convert the nitrogen of the substance to be analysed into chloride of ammonium, instead of bichloride of platinum and chloride of ammonium: we again conduct the process with absolute accuracy, and obtain from 0·300 of the substance under examination, 0·2394 of chloride of ammonium, corresponding to 0·0627 of nitrogen, or 20·90 per cent.

Now, let us assume a loss of 10 milligrammes to have occurred in each process:—this will alter the result, in the first instance, from 1·000 to 0·990 of bichloride of platinum and chloride of ammonium, corresponding to 0·062073 of nitrogen, or 20·69 per cent.; the loss of nitrogen will therefore be 20·90 − 20·69 = 0·21.

In the second instance the result will be altered from 0·2394 to 0·2294 of chloride of ammonium, corresponding to 0·0601 of nitrogen, or 20·03 per cent. The loss in this case will consequently amount to 0·87.

We see here that the same error occasions, in the one case, a loss of 0·21 per cent., with respect to the amount of nitrogen; whilst, in the other case, the loss amounts to 0·87 per cent.

We will now proceed to enumerate and examine those combinations of various substances which are best adapted for their quantitative determination. The description given of the external form and appearance of the new compounds relates more particularly to the state in which they are obtained in our analyses. With regard to the properties of the new compounds, we shall confine ourselves to the enumeration of those which bear upon the special object we have more immediately in view.

A.—FORMS AND COMBINATIONS IN WHICH THE VARIOUS BASES ARE SEPARATED FROM OTHER BODIES, OR IN WHICH THEIR WEIGHT IS DETERMINED.

BASES OF THE FIRST GROUP.

§ 68.

1. POTASSA.

The combinations best suited for the weighing of potassa are, SULPHATE OF POTASSA, NITRATE OF POTASSA, CHLORIDE OF POTASSIUM, BICHLORIDE OF PLATINUM AND CHLORIDE OF POTASSIUM (Potassio-Bichloride of Platinum).

a. Sulphate of potassa crystallizes usually in small, hard, oblique, four-sided prisms, or in double six-sided pyramids; in the analytical process it is obtained as a white crystalline mass. It dissolves with some difficulty in water, 1 part requiring 10 parts of water of 53·6° Fahrenheit; it is almost absolutely insoluble in pure alcohol, but slightly more soluble in alcohol containing sulphuric acid (Experiment No. 6). It does not affect vegetable colors; it is unalterable in the air. The crystals decrepitate strongly when heated, yielding at the same time a little water, which they hold mechanically confined. The decrepitation of crystals that have been kept long drying is less marked. At a strong red heat, sulphate of potassa fuses unaltered, and without volatilizing. When exposed to a red heat, in conjunction with chloride of ammonium, sulphate of potassa is partly, and, upon repeated application of the process, wholly, converted, with effervescence, into chloride of potassium (*H. Rose*).

COMPOSITION.

$$\begin{array}{lcrcrcr} KO & = & 588{\cdot}86 & = & 47{\cdot}11 & = & 54{\cdot}08 \\ SO_3 & = & 500{\cdot}00 & = & 40{\cdot}00 & = & 45{\cdot}92 \\ \hline & & 1088{\cdot}86 & = & 87{\cdot}11 & = & 100{\cdot}00 \end{array}$$

Bisulphate of potassa ($KO, SO_3 + HO, SO_3$), which is always produced when the neutral salt is evaporated to dryness with free sulphuric acid, is readily soluble in water, and fusible even at a moderate heat. At a red heat, it loses half its sulphuric acid, together with the basic water, but not readily—the complete reconversion of the acid into the neutral salt requiring the long-continued application of an intense red heat. However, when heated in an atmosphere of carbonate of ammonia—which may be readily procured by repeatedly throwing into the faint red-hot crucible containing the bisulphate, small lumps of pure bicarbonate of ammonia, and putting on the lid—the acid salt changes readily and quickly to the neutral sulphate. The transformation may be considered complete as soon as the salt, which was so readily fusible before, re-assumes the solid state, at a faint red heat.

b. Nitrate of potassa crystallizes generally in long six-sided striated prisms. In analysis it is obtained as a white crystalline mass; it is readily soluble in water, nearly insoluble in absolute alcohol, and sparingly soluble in spirit of wine. It does not effect vegetable colors, and is unalterable in the air. On being exposed to a gentle heat, far below redness, it fuses unaltered and without any diminution of weight; upon the application of a stronger heat, it changes into nitrite of potassa, with evolution of oxygen; and if the heat be increased to very intense redness, it becomes converted into caustic potassa, with evolution of oxygen and nitrogen. When exposed to a red heat, with chloride of ammonium, it is readily and completely converted into chloride of potassium. When repeatedly evaporated with oxalic acid in excess, it is completely converted into oxalate of potassa.

COMPOSITION.

$$\begin{array}{lcrcrcr} KO & = & 588{\cdot}86 & = & 47{\cdot}11 & = & 46{\cdot}59 \\ NO_5 & = & 675{\cdot}06 & = & 54{\cdot}00 & = & 53{\cdot}41 \\ \hline & & 1263{\cdot}92 & = & 101{\cdot}11 & = & 100{\cdot}00 \end{array}$$

c. Chloride of potassium crystallizes usually in cubes, often lengthened to columns; rarely in octahedra. In the analytical process we obtain it either in the former shape, or as a crystalline mass. It is readily soluble in water, but much less so in dilute hydrochloric acid; in absolute alcohol it is nearly insoluble, and but slightly soluble in spirit of wine. It does not affect vegetable colors, and is unalterable in the air. When heated, it decrepitates, unless it has been kept long drying, with expulsion of a little water mechanically confined in it. At a moderate red heat, it fuses unaltered and without diminution of weight; when exposed to a higher temperature, it volatilizes in white fumes; this volatilization proceeds the more slowly, the more effectually the access of air is prevented (Experiment No. 7). When repeatedly evaporated with solution of oxalic acid in excess, it is converted into oxalate of potassa.

COMPOSITION.

$$\begin{array}{lcrcrcr} K & = & 488{\cdot}86 & = & 39{\cdot}11 & = & 52{\cdot}44 \\ Cl & = & 443{\cdot}28 & = & 35{\cdot}46 & = & 47{\cdot}56 \\ \hline & & 932{\cdot}14 & = & 74{\cdot}57 & = & 100{\cdot}00 \end{array}$$

d. Bichloride of platinum and chloride of potassium (Potassio-bichloride of Platinum) presents either small reddish-yellow octahedra, or a lemon-colored powder. It is difficultly soluble in cold, but more readily so in hot water; nearly insoluble in absolute alcohol, and but sparingly soluble in spirit of wine—one part requiring for its solution, respectively, 12083 parts of absolute alcohol, 3775 parts of spirit of wine of 76 per cent.—1053 parts of spirit of wine of 55 per cent. (Experiment No. 8, *a*). Presence of free hydrochloric acid sensibly increases the solubility (Experiment No. 8, *b*). In caustic potassa it dissolves completely to a yellow fluid. It is unalterable in the air, and at 212° F. On exposure to an intense red heat, the whole of the chlorine which was combined with the platinum escapes, metallic platinum and chloride of potassium being left; but even after long-continued fusion, there remains always a little potassio-bichloride of platinum which resists decomposition. Complete decomposition is effected, however, by heating the double salt to redness in a current of hydrogen gas, or with some oxalic acid.

According to *Andrews*, the bichloride of platinum and chloride of potassium, even though dried at a temperature considerably exceeding 212° F., retains still 0·0055 of its weight of water.

COMPOSITION.

$$\begin{aligned}
K &= 488{\cdot}86 = 39{\cdot}11 = 16{\cdot}00 \\
Pt &= 1236{\cdot}75 = 98{\cdot}94 = 40{\cdot}48 \\
3\,Cl &= 1329{\cdot}84 = 106{\cdot}38 = 43{\cdot}52 \\
\hline
& \quad 3055{\cdot}45 = 244{\cdot}43 = 100{\cdot}00
\end{aligned}$$

$$\begin{aligned}
K\,Cl &= 932{\cdot}14 = 74{\cdot}57 = 30{\cdot}51 \\
Pt\,Cl_2 &= 2123{\cdot}31 = 169{\cdot}86 = 69{\cdot}49 \\
\hline
& \quad 3055{\cdot}45 = 244{\cdot}43 = 100{\cdot}00
\end{aligned}$$

§ 69.

2. SODA.

Soda is usually weighed as SULPHATE OF SODA, NITRATE OF SODA, CHLORIDE OF SODIUM, or CARBONATE OF SODA. It is separated from potassa in the form of SODIO-BICHLORIDE OF PLATINUM.

a. The anhydrous neutral *sulphate of soda* is a white powder or a white very friable mass. It dissolves readily in water ; but is sparingly soluble in absolute alcohol ; presence of free sulphuric acid slightly increases its solubility in that menstruum ; it is somewhat more readily soluble in spirit of wine (Experiment No. 9). The presence of free sulphuric acid increases its solubility in absolute alcohol. It does not affect vegetable colors ; upon exposure to moist air, it slowly absorbs water (Experiment No. 10). The application of a gentle heat leaves it unaltered : upon exposure to an intense red heat, it fuses, without decomposition or diminution of weight. When heated to redness with chloride of ammonium, it comports itself the same as sulphate of potassa under similar circumstances.

COMPOSITION.

$$\begin{aligned}
Na\,O &= 387{\cdot}44 = 31 = 43{\cdot}66 \\
S\,O_3 &= 500{\cdot}00 = 40 = 56{\cdot}34 \\
\hline
& \quad 887{\cdot}44 = 71 = 100{\cdot}00
\end{aligned}$$

Bisulphate of soda ($Na\,O, S\,O_3 + H\,O, S\,O_3$), which is always produced upon the evaporation of a solution of the neutral salt with sulphuric acid in excess, fuses even at a gentle heat ; it may be readily converted into the neutral salt, in the same manner as the bisulphate of potassa is converted into the neutral sulphate (see § 68, *a*).

b. Nitrate of soda crystallizes in obtuse rhombohedra. In analysis it is generally obtained as an amorphous mass. It dissolves readily in water, but is almost insoluble in absolute alcohol, and but little more soluble in spirit of wine. It does not affect vegetable colors, and is unalterable in the air under common circumstances ; but when exposed to very moist air, it absorbs water. It fuses without decomposition at a temperature far below red heat ; at a higher temperature it undergoes the same decomposition as nitrate of potassa (see § 68, *b*, comp. Experiment No. 11). When heated to redness, in conjunction with chloride of ammonium, or evaporated with solution of oxalic acid, it comports itself like the corresponding potassa salt under similar circumstances.

COMPOSITION.

$$\begin{array}{lrrr} NaO & = 387{\cdot}44 & = 31 & = 36{\cdot}47 \\ NO_5 & = 675{\cdot}06 & = 54 & = 63{\cdot}53 \\ \hline & 1062{\cdot}50 & = 85 & = 100{\cdot}00 \end{array}$$

c. Chloride of sodium crystallizes in cubes, octahedra, and hollow four-sided pyramids. In the analytical process it is frequently obtained as an amorphous mass. It dissolves readily in water, but is much less soluble in dilute hydrochloric acid; it is nearly insoluble in absolute alcohol, and but sparingly soluble in spirit of wine. 100 parts of spirit of wine of 75 per cent. dissolve, at a temperature of 59° Fahr., 0·7 part (*Wagner*). It is neutral to vegetable colors. Exposed to a somewhat moist atmosphere, it slowly absorbs water (Experiment No. 12). Crystals of this salt that have been kept drying a considerable time decrepitate when heated, yielding a little water, which they hold mechanically confined. The salt fuses at a red heat without decomposition; at a white heat, and, in open vessels even at a bright red heat, it volatilizes in white fumes (Experiment No. 13). Upon evaporation and ignition with oxalic acid or oxalate of ammonia, it comports itself like the corresponding salt of potassa.

COMPOSITION.

$$\begin{array}{lrrr} Na & = 287{\cdot}44 & = 23{\cdot}00 & = 39{\cdot}34 \\ Cl & = 443{\cdot}28 & = 35{\cdot}46 & = 60{\cdot}66 \\ \hline & 730{\cdot}72 & = 58{\cdot}46 & = 100{\cdot}00 \end{array}$$

d. Anhydrous *carbonate of soda* is a white powder or a white friable mass. It dissolves readily in water, but much less so in solution of ammonia (*Margueritte*); it is insoluble in alcohol. Its reaction is strongly alkaline. Exposed to the air, it absorbs water very slowly. At a strong red heat, it fuses without decomposition, and without volatilizing.

COMPOSITION.

$$\begin{array}{lrrr} NaO & = 387{\cdot}44 & = 31 & = 58{\cdot}49 \\ CO_2 & = 275{\cdot}00 & = 22 & = 41{\cdot}51 \\ \hline & 662{\cdot}44 & = 53 & = 100{\cdot}00 \end{array}$$

e. Sodio-bichloride of platinum crystallizes with 6 equivalents of water ($NaCl, PtCl_2 + 6\,aq.$), in light yellow, transparent, prismatic crystals, which dissolve readily both in water and in spirit of wine.

§ 70.

3. Ammonia (NH_4O).

Ammonia is most appropriately weighed as CHLORIDE OF AMMONIUM, or as BICHLORIDE OF PLATINUM AND CHLORIDE OF AMMONIUM (ammonio-bichloride of platinum).

Under certain circumstances, ammonia may also be estimated from the volume of the nitrogen eliminated from it; in many cases it may be determined also by passing the liberated ammonia into a standard acid solution (*Peligot*).

a. Chloride of ammonium crystallizes in cubes and octahedra, but more frequently in feathery crystals. In analysis we obtain it uniformly as a white mass. It dissolves readily in water, but is difficultly soluble in spirit of wine. It does not alter vegetable colors, and remains unaltered in the air. Solution of chloride of ammonium, when evaporated in the water-bath, loses a small quantity of ammonia, and becomes slightly acid. The diminution of weight occasioned by this loss of ammonia is very trifling (Experiment No. 14). At 212° F. chloride of ammonium loses nothing, or very little of its weight (Experiment No. 14). At a higher temperature it volatilizes readily, and without undergoing decomposition.

COMPOSITION.

$$\begin{array}{lrrr} N\,H_4 & = 225{\cdot}06 = & 18{\cdot}00 = & 33{\cdot}67 \\ Cl & = 443{\cdot}28 = & 35{\cdot}46 = & 66{\cdot}33 \\ \hline & 668{\cdot}34 = & 53{\cdot}46 = & 100{\cdot}00 \end{array}$$

$$\begin{array}{lrrr} N\,H_3 & = 212{\cdot}56 = & 17{\cdot}00 = & 31{\cdot}80 \\ C\,Hl & = 455{\cdot}78 = & 36{\cdot}46 = & 68{\cdot}20 \\ \hline & 668{\cdot}34 = & 53{\cdot}46 = & 100{\cdot}00 \end{array}$$

b. Bichloride of platinum and chloride of ammonium (ammonio-bichloride of platinum) occurs either as a heavy, lemon-colored powder or in small, hard octahedral crystals of a bright yellow color. It is difficultly soluble in cold, but more readily in hot water. It is very sparingly soluble in absolute alcohol, but more readily in spirit of wine—1 part requiring, of absolute alcohol, 26535 parts; of spirit of wine of 76 per cent., 1406 parts; of spirit of wine of 55 per cent., 665 parts. The presence of free acid sensibly increases its solubility (Experiment No. 15). It remains unaltered in the air, and at 212° F. Upon exposure to a red-heat, chlorine and chloride of ammonium escape, leaving the metallic platinum as a porous mass (spongy platinum). However, if due care be not taken, in this process, to apply the heat gradually, the escaping fumes will carry off particles of platinum, which will coat the lid of the crucible.

COMPOSITION.

$$\begin{array}{lrrr} N\,H_4 & = 225{\cdot}06 = & 18{\cdot}00 = & 8{\cdot}06 \\ Pt & = 1236{\cdot}75 = & 98{\cdot}94 = & 44{\cdot}30 \\ 3\,Cl & = 1329{\cdot}84 = & 106{\cdot}38 = & 47{\cdot}64 \\ \hline & 2791{\cdot}65 = & 223{\cdot}32 = & 100{\cdot}00 \end{array}$$

$$\begin{array}{lrrr} N\,H_4\,Cl & = 668{\cdot}34 = & 53{\cdot}46 = & 23{\cdot}94 \\ Pt\,Cl_2 & = 2123{\cdot}31 = & 169{\cdot}86 = & 76{\cdot}06 \\ \hline & 2791{\cdot}65 = & 223{\cdot}32 = & 100{\cdot}00 \end{array}$$

$$\begin{array}{lrrr} N\,H_3 & = 212{\cdot}56 = & 17{\cdot}00 = & 7{\cdot}61 \\ H\,Cl & = 455{\cdot}78 = & 36{\cdot}46 = & 16{\cdot}33 \\ Pt\,Cl_2 & = 2123{\cdot}31 = & 169{\cdot}86 = & 76{\cdot}06 \\ \hline & 2791{\cdot}65 = & 223{\cdot}32 = & 100{\cdot}00 \end{array}$$

$$\begin{array}{lrrr}
N & = 175{\cdot}06 = & 14{\cdot}00 = & 6{\cdot}27 \\
H_4 & = 50{\cdot}00 = & 4{\cdot}00 = & 1{\cdot}79 \\
Pt & = 1236{\cdot}75 = & 98{\cdot}94 = & 44{\cdot}30 \\
Cl_3 & = 1329{\cdot}84 = & 106{\cdot}38 = & 47{\cdot}64 \\
\hline
 & 2791{\cdot}65 = & 223{\cdot}32 = & 100{\cdot}00
\end{array}$$

c. *Nitrogen gas* is colorless, tasteless, and inodorous; it mixes with air, without producing the slightest coloration; it does not affect vegetable colors. Its specific gravity is 0·96743 (air = 1). One litre (one cubic decimeter) weighs at 32° F., and 29·8 of the barometer, 1·25107 grm. It is difficultly soluble in water, 1 volume of water absorbing, at 32° F., and 29·8 of the barometer, 0·02035 vol.; at 50° F., 0·01607 vol.; at 59° F., 0·01478 vol. of nitrogen gas (*Bunsen*).

BASES OF THE SECOND GROUP.

§ 71.

1. BARYTA.

Baryta is generally weighed as SULPHATE OF BARYTA, CARBONATE OF BARYTA, and SILICO-FLUORIDE OF BARIUM.

a. Artificially prepared *sulphate of baryta* presents the appearance of a fine white powder. When recently precipitated, it is difficult to obtain a clear filtrate, especially if the precipitation was effected without the aid of heat, and the solution contains neither hydrochloric acid nor chloride of ammonium. It is insoluble in cold and in hot water. It has a great tendency, upon precipitation, to carry down with it other substances contained in the solution from which it separates, more particularly nitrate of baryta, chloride of barium, sesquioxide of iron, &c. These substances can generally be completely removed only after ignition, by washing with appropriate solvents. Even the precipitate obtained from a solution of chloride of barium by means of sulphuric acid in excess contains traces of chloride of barium, which it is impossible to remove, even by washing with boiling water, but which are dissolved by nitric acid (*Siegle*). Cold dilute acids dissolve trifling, yet appreciable traces of sulphate of baryta; for instance, 1000 parts of nitric acid of 1·032 sp. gr. dissolve 0·062 parts of $Ba\,O, S\,O_3$. Cold concentrated acids dissolve considerably more; thus, 1000 parts of nitric acid of 1·167 sp. gr. dissolve 2 parts of $Ba\,O, S\,O_3$ (*Calvert*). Boiling hydrochloric acid also dissolves appreciable traces; thus 230 cub. centimet. of hydrochloric acid of 1·02 sp. gr. were found, after a quarter of an hour's boiling with 0·679 grm. of sulphate of baryta, to have dissolved of it 0·048 grm. Acetic acid dissolves less sulphate of baryta than the other acids; thus, 80 cub. centimet. of acetic acid of 1·02 sp. gr. were found, after a quarter of an hour's boiling with 0·4 grm. of $Ba\,O, S\,O_3$, to have dissolved only 0·002 grm. (*Siegle*). Several of the salts also increase the solubility of sulphate of baryta; I have found this to be the case, more epecially, with chloride of magnesium. Sulphate of baryta remains quite unaltered in the air, at 212° F., and even at a red heat. When heated to redness, mixed with charcoal, in a covered crucible, it is reduced to sulphide of barium; free access of air prevents this reduction taking place. Upon exposure to a red heat, mixed with chloride of ammonium, sulphate of baryta undergoes partial decomposition. Cold solutions of alkaline bicarbonates or of carbonate of ammonia fail to decompose sulphate of baryta; cold solutions of the simple carbonates of the fixed alkalies have only a slight decomposing action upon it; but boiling solutions of the simple carbonates of the fixed alkalies effect, upon repeated application, at last the complete decomposition of the salt (*H. Rose*). By fusion with alkaline carbonates, sulphate of baryta is readily decomposed.

COMPOSITION.

$$\begin{array}{lcl}
Ba\,O & = & 957{\cdot}32 = 76{\cdot}59 = 65{\cdot}69 \\
S\,O_3 & = & 500{\cdot}00 = 40{\cdot}00 = 34{\cdot}31 \\
\hline
 & & 1457{\cdot}32 = 116{\cdot}59 = 100{\cdot}00
\end{array}$$

b. Artificially prepared *carbonate of baryta* presents the appearance of a white powder. It dissolves in 14137 parts of cold, and in 15421 parts of boiling water (Experiment No. 16). It dissolves far more readily in solutions of chloride of ammonium or nitrate of ammonia; from these solutions it is, however, precipitated again, though not completely, by caustic ammonia. In water containing free carbonic acid, carbonate of baryta dissolves, being converted into bicarbonate. In water containing ammonia and carbonate of ammonia, it is nearly insoluble, one part requiring 141000 parts (Experiment No. 17).

Solution of carbonate of baryta has a very faint alkaline reaction. Carbonate of baryta is unalterable in the air, and at a red heat. When exposed to the strongest heat of a blast-furnace, it slowly yields up the whole of its carbonic acid; this expulsion of the carbonic acid is promoted by the simultaneous action of aqueous vapor. Upon heating it to redness with charcoal, caustic baryta is formed, with evolution of carbonic oxide gas.

COMPOSITION.

$$\begin{array}{lcl}
Ba\,O & = & 957{\cdot}32 = 76{\cdot}59 = 77{\cdot}69 \\
C\,O_2 & = & 275{\cdot}00 = 22{\cdot}00 = 22{\cdot}31 \\
\hline
 & & 1232{\cdot}32 = 98{\cdot}59 = 100{\cdot}00
\end{array}$$

c. Silico-fluoride of barium forms small, hard, and colorless crystals, or (more generally) a crystalline powder. It dissolves in 3800 parts of cold water; in hot water it is more readily soluble (Experiment No. 18). The presence of free hydrochloric acid increases its solubility considerably (Experiment No. 19). In spirit of wine it is almost insoluble. It is unalterable in the air, and at 212° F.; when heated to redness, it is decomposed into bifluoride of silicon, which escapes, and fluoride of barium, which remains.

COMPOSITION.

$$\begin{array}{lcl}
Ba\,Fl & = & 1094{\cdot}82 = 87{\cdot}59 = 62{\cdot}39 \\
Si\,Fl_2 & = & 660{\cdot}18 = 52{\cdot}81 = 37{\cdot}61 \\
\hline
 & & 1755{\cdot}00 = 140{\cdot}40 = 100{\cdot}00
\end{array}
\qquad
\begin{array}{lcl}
Ba & = & 857{\cdot}32 = 68{\cdot}59 = 48{\cdot}85 \\
Si & = & 185{\cdot}18 = 14{\cdot}81 = 10{\cdot}55 \\
Fl_3 & = & 712{\cdot}50 = 57{\cdot}00 = 40{\cdot}60 \\
\hline
 & & 1755{\cdot}00 = 140{\cdot}40 = 100{\cdot}00
\end{array}$$

§ 72.

2. STRONTIA.

Strontia is weighed either as SULPHATE OF STRONTIA, or as CARBONATE OF STRONTIA.

a. Sulphate of strontia, artificially prepared, is a white powder. It dissolves in 6895 parts of cold, and 9638 parts of boiling water (Experiment No. 20). In water containing sulphuric acid, it is still more difficultly soluble, requiring from 11000 to 12000 parts (Experiment No. 21). Of cold hydrochloric acid of 8·5 per cent., it requires 474 parts; of cold nitric acid of 4·8 per cent., 432 parts; of cold acetic acid ($\bar{A}$, H O) of 15·6 per cent., as much as 7843 parts (Experiment No. 22). It dissolves in solution of chloride of sodium, but is precipitated again from this solution by sulphuric acid. It is nearly insoluble both in absolute alcohol and in weak spirit of wine. It does not alter vegetable colors; and remains unaltered in the air, and at a red heat. When exposed to a most intense red heat, it fuses without undergoing decomposition. When mixed with charcoal, and heated to redness, in a closely-covered crucible, it is reduced to sulphide of strontium. The solutions of carbonates and bicarbonates of potassa, soda, and ammonia decompose sulphate of strontia completely at the common temperature, and even though considerable quantities of alkaline sulphates be present (*H. Rose*). Boiling promotes the decomposition.

COMPOSITION.

$$\begin{array}{rcl} \mathrm{Sr\,O} = & 645{\cdot}93 = 51{\cdot}67 = & 56{\cdot}37 \\ \mathrm{S\,O_3} = & 500{\cdot}00 = 40{\cdot}00 = & 43{\cdot}63 \\ \hline & 1145{\cdot}93 = 91{\cdot}67 = & 100{\cdot}00 \end{array}$$

b. Carbonate of strontia, artificially prepared, is a white, light, loose powder. It dissolves, at the common temperature, in 18045 parts of water (Experiment No. 23). Presence of ammonia diminishes its solubility (Experiment No. 24). It dissolves pretty readily in solutions of chloride of ammonium and of nitrate of ammonia, but is precipitated again from these solutions by ammonia, and carbonate of ammonia, and more completely than carbonate of baryta under similar circumstances. Water impregnated with carbonic acid dissolves it as a bicarbonate. Its reaction is very feebly alkaline. It remains unaltered in the air, and even at a red heat; but when exposed to a most intense red heat, it fuses and gradually loses its carbonic acid. Upon heating it to intense redness with charcoal, caustic strontia is formed, with evolution of carbonic oxide gas.

COMPOSITION.

$$\begin{array}{rcl} \mathrm{Sr\,O} = & 645{\cdot}93 = 51{\cdot}67 = & 70{\cdot}14 \\ \mathrm{C\,O_2} = & 275{\cdot}00 = 22{\cdot}00 = & 29{\cdot}86 \\ \hline & 920{\cdot}93 = 73{\cdot}67 = & 100{\cdot}00 \end{array}$$

§ 73.

3. LIME.

Lime is weighed either as SULPHATE OF LIME, or as CARBONATE OF

LIME; to convert it into the latter form, it is first precipitated as oxalate of lime.

a. Artificially prepared anhydrous *sulphate of lime* is a loose, white powder. It dissolves, at the common temperature, in 430 parts, at 212° F., in 460 parts of water (*Poggiale*). Presence of hydrochloric acid, nitric acid, chloride of ammonium, sulphate of soda, and chloride of sodium, increases its solubility. The aqueous solution of sulphate of lime does not alter vegetable colors. In alcohol and in spirit of wine of 90 per cent. it is almost absolutely insoluble. Exposed to the air, it slowly absorbs water. It remains unaltered at a dull red heat. Heated to intense bright redness, it fuses without undergoing decomposition. When mixed with charcoal, and heated to redness, in a covered crucible, it is reduced to sulphide of calcium. Solutions of akaline carbonates and bicarbonates decompose sulphate of lime more readily still than sulphate of strontia.

COMPOSITION.

$$\begin{array}{lr} CaO = 350 = 28 = & 41{\cdot}18 \\ SO_3 = 500 = 40 = & 58{\cdot}82 \\ \hline 850 = 68 = & 100{\cdot}00 \end{array}$$

b. Artificially prepared *carbonate of lime* is a fine white powder. It dissolves in 10601 parts of cold (Experiment No. 25), and in 8834 parts of boiling water (Experiment No. 26). The aqueous solution has a barely perceptible alkaline reaction. In water containing ammonia and carbonate of ammonia, it dissolves still more sparingly, one part of the salt requiring 65000 parts of the solvent (Experiment No. 27); this solution is not precipitated by oxalate of ammonia. Presence of chloride of ammonium and of nitrate of ammonia increases the solubility of carbonate of lime; but the salt is precipitated again from these solutions by ammonia and carbonate of ammonia, and more completely than carbonate of baryta under similar circumstances. Neutral salts of potassa and soda likewise increase its solubility. Water impregnated with carbonic acid dissolves carbonate of lime as a bicarbonate. Carbonate of lime remains unaltered in the air, at 212° F.; and even at a low red heat; but upon the application of an intense red heat, more particularly with free access of air, it gradually loses its carbonic acid. By means of a gas blowpipe-lamp, carbonate of lime (about 0·5 grm.), in an open platinum crucible, is without difficulty reduced to the caustic state; attempts to effect complete reduction over a spirit lamp with double draught have, however, failed (Experiment No. 28). It is decomposed far more readily when mixed with charcoal and heated to redness, giving off its carbonic acid, in the form of carbonic oxide.

COMPOSITION.

$$\begin{array}{lr} CaO = 350{\cdot}00 = 28 = & 56{\cdot}00 \\ CO_2 = 275{\cdot}00 = 22 = & 44{\cdot}00 \\ \hline 625{\cdot}00 = 50 = & 100{\cdot}00 \end{array}$$

c. *Oxalate of lime*, precipitated from hot or concentrated solutions, is a fine white powder consisting of infinitely minute indistinct crystals, and almost absolutely insoluble in water. If the oxalic acid is held to be monobasic, the salt has the formula $CaO, C_2O_3 + aq$. When precipitated from cold, extremely dilute solutions, the salt presents a more distinctly crystalline appearance, and consists of a mixture of $CaO, C_2O_3 + aq.$, and $CaO, C_2O_3 + 3\ aq.$ (*Souchay* and *Lenssen*). Presence of free oxalic acid and acetic acid slightly increases the solubility of oxalate of lime. The stronger acids (hydrochloric acid, nitric acid) dissolve it readily; from these solutions it is precipitated again unaltered, by alkalies; and also by alkaline oxalates or alkaline acetates added in excess (provided always the excess of acid be not too great). Oxalate of lime does not dissolve in solutions of chloride of potassium, chloride of sodium, chloride of ammonium, chloride of barium, chloride of calcium, and chloride of strontium, even though these solutions be hot and concentrated; but, on the other hand, it dissolves readily, and in appreciable quantities, in hot solutions of the salts belonging to the magnesia group. From these solutions it is reprecipitated by an excess of alkaline oxalate (*Souchay* and *Lenssen*). When treated with solutions of many of the heavy metals, *e.g.*, with solution of chloride of copper, nitrate of silver, &c., oxalate of lime suffers decomposition, a soluble salt of lime being formed, and an oxalate of the heavy metallic oxide, which separates immediately, or after some time (*Reynoso*). Oxalate of lime is unalterable in the air, and at 212° F. Dried at the latter temperature, it has invariably the following composition (Experiment No. 29, and also *Souchay* and *Lenssen*, "Annal. der Chem. und Pharm." 100, 322):—

$$
\begin{array}{lrrr}
CaO & = 350{\cdot}00 = & 28 = & 38{\cdot}36 \\
C_2O_3 & = 450{\cdot}00 = & 36 = & 49{\cdot}32 \\
1\ aq. & = 112{\cdot}50 = & 9 = & 12{\cdot}32 \\
\hline
 & 912{\cdot}50 = & 73 = & 100{\cdot}00
\end{array}
$$

At a temperature of from 356° to 392° F., oxalate of lime loses its water, without undergoing decomposition; at a somewhat higher temperature, still scarcely reaching incipient dull redness, it is decomposed, without actual separation of carbon, into carbonic oxide, which escapes, and carbonate of lime, which remains. The powder, which was previously of snowy whiteness, transiently assumes a gray color in the course of this process, even though the oxalate be perfectly pure. Upon continued application of heat, this gray color disappears again. If the oxalate of lime is heated in small coherent fragments, such as are obtained upon drying the precipitated salt on a filter, the commencement and progress of the decomposition can be readily traced by this transient appearance of gray. If the process of heating be conducted properly, the residue will not contain a trace of caustic lime.

§ 74.

4. MAGNESIA.

Magnesia is weighed as SULPHATE OF MAGNESIA, PYROPHOSPHATE OF MAGNESIA, OR PURE MAGNESIA. To convert it into the pyrophosphate, it is precipitated as BASIC PHOSPHATE OF AMMONIA AND MAGNESIA.

a. Anhydrous sulphate of magnesia presents the appearance of a white opaque mass. It dissolves readily in water. It is nearly altogether insoluble in absolute alcohol, and but very sparingly soluble in spirit of wine. It does not alter vegetable colors. Exposed to the air, it absorbs water rapidly. At a moderate red heat, it remains unaltered; but when heated to intense redness, it undergoes partial decomposition, losing part of its acid, after which it is no longer perfectly soluble in water. By means of a blowpipe-lamp, it is tolerably easy to expel the whole of the sulphuric acid from small quantities of sulphate of magnesia (Experiment No. 30). Ignited with chloride of ammonium, sulphate of magnesia is not decomposed.

COMPOSITION.

$$
\begin{array}{lllll}
Mg\,O & = 250{\cdot}19 & = 20 & = & 33{\cdot}33 \\
S\,O_3 & = 500{\cdot}00 & = 40 & = & 66{\cdot}67 \\
\hline
 & 750{\cdot}19 & = 60 & = & 100{\cdot}00
\end{array}
$$

b. Basic phosphate of magnesia and ammonia is a white crystalline powder. It dissolves, at the common temperature, in 15293 parts of cold water (Experiment No. 31). In water containing ammonia, it is much more difficultly soluble—one part of the salt requiring 45000 parts of the solvent (Experiment No. 32). Chloride of ammonium slightly increases its solubility (Experiments No. 34 and 35). Presence of alkaline phosphates exercises no influence in this respect. The basic phosphate of magnesia and ammonia dissolves readily in acids, even in acetic acid. Its composition is expressed by the formula

$$2\,Mg\,O,\,N\,H_4O,\,P\,O_5 + 12\text{ aq.}$$

10 of the 12 equivalents of water escape at 212° F., the remaining 2, together with the ammonia, at a red heat, leaving $2\,Mg\,O,\,P\,O_5$. The change of the phosphoric to pyrophosphoric acid, is indicated by a vivid incandescence of the whole mass.

Ammonia precipitates phosphate of magnesia and ammonia from its solution in dilute hydrochloric or dilute nitric acid, to the extent corresponding with the degree of solubility of that salt in water impregnated with ammonia, or with ammonia and an ammoniacal salt. *Weber* (Pogg. 73, p. 152) having questioned the correctness of this fact, I was induced to test it again by experiment (No. 33) which, however, yielded exactly the same results as before.

c. Pyrophosphate of magnesia presents the appearance of a white mass, often slightly inclining to gray. It is barely soluble in water, but readily so in hydrochloric acid, and in nitric acid. It remains unaltered in the air, and even at a red heat; at a very intense red heat it fuses unaltered. It leaves the color of moist turmeric, and of reddened litmus paper unchanged.

If we dissolve pyrophosphate of magnesia in hydrochloric or nitric acid, add water to the solution, boil for some time, and then precipitate with ammonia in excess, we obtain a precipitate of phosphate of magnesia and ammonia which, after ignition, gives less weight of $2\,Mg\,O,\,P\,O_5$, than corresponds with the amount of substance used. *Weber* gives the loss as from 1·3 to 2·3 per cent. My own experiments (No. 36) confirm this statement, and point out the circumstances under which the loss is the least considerable (compare also § 135). By long-continued fusion, with carbonate of potassa and soda, pyrophosphate of magnesia is completely decomposed, the phosphoric acid being reconverted into the tribasic state. If, therefore, we treat the fused mass with hydrochloric acid, add water and ammonia, and heat the precipitate to redness, we re-obtain the whole quantity of the salt used.

COMPOSITION.

$$\begin{array}{llll} 2MgO = & 500{\cdot}38 = & 40{\cdot}00 = & 36{\cdot}04 \\ PO_5 \;\; = & 887{\cdot}50 = & 71{\cdot}00 = & 63{\cdot}96 \\ \hline & 1387{\cdot}88 = & 111{\cdot}00 = & 100{\cdot}00 \end{array}$$

d. Pure magnesia is a white, light, loose powder. It dissolves in 55368 parts of cold, and in the same proportion of boiling water (Experiment No. 37). Its aqueous solution has a very slightly alkaline reaction. Magnesia dissolves in hydrochloric acid, and in other acids, without evolution of gas. Exposed to the air, it slowly absorbs carbonic acid and water. Magnesia is highly infusible, remaining unaltered at a strong red heat, and fusing superficially only at the very highest temperature.

COMPOSITION.

$$\begin{array}{llll} Mg = & 150{\cdot}19 = & 12 = & 60{\cdot}03 \\ O \;\; = & 100{\cdot}00 = & 8 = & 39{\cdot}97 \\ \hline & 250{\cdot}19 = & 20 = & 100{\cdot}00 \end{array}$$

BASES OF THE THIRD GROUP.

§ 75.

1. ALUMINA.

Alumina is usually precipitated as HYDRATE OF ALUMINA, and always weighed in the pure state.

a. Hydrate of alumina, recently precipitated, is a gelatinous mass, which invariably retains a minute proportion of the acid with which the alumina was combined previous to precipitation, as well as of the alkali which has served as the precipitant; it is freed with difficulty from these admixtures by repeated washing.

Hydrate of alumina is insoluble in pure water; but it readily dissolves in solutions of soda or potassa, and in ethylamine (*Sonnenschein*); it is sparingly soluble in caustic ammonia, and altogether insoluble in carbonate of ammonia; presence of ammoniacal salts greatly diminishes its solubility in caustic ammonia (Experiment No. 38). The correctness of this statement of mine in the first edition of the present work, has been amply confirmed since by *Malaguti* and *Durocher* ("Ann. de Chim. et de Phys.," 3 Ser. 16, 421); and also by experiments made by my former assistant, *Mr. J. Fuchs*. The former chemists (*Malaguti* and *Durocher*) state also that, when a solution of alumina is precipitated with sulphide of ammonium, the fluid may be filtered off five minutes after, without a trace of alumina in it. *Fuchs* did not find this to be the case (Experiment No. 39).

Hydrate of alumina, recently precipitated, dissolves readily in hydrochloric or nitric acid; but after filtration, or after having remained for some time in the fluid from which it has been precipitated, it dissolves in these acids with much greater difficulty, and only after long digestion. Hydrate of alumina shrinks considerably upon desiccation, and, when dry, becomes a hard, transparent, yellowish, or a white, earthy mass. When heated to redness, it loses its water, and this loss is frequently attended with slight decrepitation, and invariably with considerable diminution of bulk.

b. Alumina, prepared by heating the hydrate to a moderate degree of redness, is a loose and soft mass; but upon the application of a very intense degree of redness, it concretes into small, hard lumps. At the most intense white heat, it fuses to a colorless glass. Ignited alumina is dissolved by dilute acids with very great difficulty; in fuming hydrochloric acid, it dissolves upon long-continued digestion in a warm place, slowly, but completely. Ignition in a current of hydrogen gas leaves it unaltered. By fusion with bisulphate of potassa, it is rendered soluble, the residue dissolving readily in hydrochloric acid and water. When alumina is fused at a very high temperature, in conjunction with ten times the quantity of carbonate of soda, aluminate of soda is formed, which is soluble in water (*R. Richter*). Placed upon moist reddened litmus paper, pure alumina does not change the color to blue. Upon igniting alumina with chloride of ammonium, chloride of aluminium escapes; but the process fails to effect complete volatilization of the alumina (*H. Rose*).

COMPOSITION.

$$\begin{array}{lcl} 2\,Al = & 340{\cdot}84 = 27{\cdot}26 = & 53{\cdot}19 \\ 3\,O \ = & 300{\cdot}00 = 24{\cdot}00 = & 46{\cdot}81 \\ \hline & 640{\cdot}84 = 51{\cdot}26 = & 100{\cdot}00 \end{array}$$

§ 76.

2. Sesquioxide of Chromium.

Sesquioxide of chromium is usually precipitated as **HYDRATED SESQUIOXIDE OF CHROMIUM**, and always weighed in the pure state.

a. Hydrated sesquioxide of chromium, recently precipitated, is a greenish-gray, gelatinous mass, insoluble in water; it dissolves readily, in the cold, in solutions of potassa or soda, to a dark-green fluid; it dissolves, also in the cold, but rather sparingly, in solution of ammonia, to a bright violet-red fluid. In acids it dissolves readily, imparting a dark-green tint to the fluid. Presence of chloride of ammonium exercises no influence upon the solubility of hydrated sesquioxide of chromium in ammonia. Boiling effects the complete separation of the sesquioxide from its solutions in potassa, soda, or ammonia (Experiment No. 40). Dried hydrated sesquioxide of chromium is a greenish-blue powder; it loses its water of hydration at a gentle red heat.

b. Sesquioxide of chromium, produced by heating the hydrate to dull redness, is a dark green powder; upon the application of a higher degree of heat, it assumes a lighter tint, but suffers no diminution of weight; the transition from the darker to the lighter tint is marked by a vivid incandescence of the powder. The feebly ignited sesquioxide is difficultly soluble in hydrochloric acid, and the strongly ignited sesquioxide is altogether insoluble in that acid. Mixed with chloride of ammonium, and exposed to a red heat, sesquioxide of chromium remains unaltered; it suffers no alteration when ignited in a current of hydrogen gas.

COMPOSITION.

$$\begin{array}{lcl} 2\,Cr = & 669{\cdot}40 = 53{\cdot}56 = & 69{\cdot}05 \\ 3\,O \ = & 300{\cdot}00 = 24{\cdot}00 = & 30{\cdot}95 \\ \hline & 969{\cdot}40 = 77{\cdot}56 = & 100{\cdot}00 \end{array}$$

BASES OF THE FOURTH GROUP.

§ 77.

1. OXIDE OF ZINC.

Zinc is always weighed in the form of oxide; it is, however, usually precipitated as BASIC CARBONATE OF ZINC, or as SULPHIDE OF ZINC.

a. Basic carbonate of zinc, recently precipitated, is a white, flocculent mass, nearly insoluble in water—(one part requiring 44600 parts—Experiment No. 42)—but readily soluble in solutions of potassa, ammonia, carbonate of ammonia, and in acids. The solutions of zinc in soda or potassa, if concentrated, are not altered by boiling; but if dilute, nearly all the oxide of zinc present is thrown down, as a white precipitate. From the solutions of ammonia also, especially if they are dilute, oxide of zinc separates upon boiling. When a neutral solution of zinc is precipitated with carbonate of soda or carbonate of potassa, carbonic acid is evolved, since the precipitate formed is not $Zn\ O, CO_2$, but consists of a mixture of hydrated oxide of zinc with carbonate of zinc, in varying proportions, according to the degree of concentration of the solution, and to the mode of precipitation. Owing to the presence and action of this carbonic acid, part of the oxide of zinc remains in solution; the cold filtered fluid yields, therefore, a precipitate when acted upon by sulphide of ammonium.

But if the solution is precipitated boiling, and kept at that temperature for some time, the precipitation of the zinc is complete to the extent that the filtrate is not rendered turbid by the addition of sulphide of ammonium; still, if the filtrate, mixed with sulphide of ammonium, be allowed to stand at rest for many hours, minute and almost imponderable flakes of sulphide of zinc will separate from the fluid. The precipitate of carbonate of zinc, obtained in the manner just described, may be completely freed from all admixture of alkali, by washing with hot water. If ammoniacal salts be present, every trace of ammonia must be expelled first, before the complete* precipitation of the zinc can be effected. If the solution of a zinc salt is mixed with carbonate of potassa or soda in excess, the mixture evaporated to dryness, at a gentle heat, and the residue treated with cold water, a perceptible proportion of the zinc is obtained in solution as carbonate of zinc and potassa or soda; but if the mixture is evaporated to dryness, at boiling heat, and the residue treated with hot water, the whole of the zinc, with the exception of an extremely minute proportion, as we have already had occasion to observe, is obtained as carbonate of zinc.

The dried basic carbonate of zinc is a fine, white, loose powder; exposure to a red heat converts it into oxide of zinc.

b. Oxide of zinc, produced from the carbonate by the application of a red heat, is a white light powder, with a slightly yellow tint When heated, it acquires a yellow color, which disappears again on cooling. Upon exposing oxide of zinc, mixed with charcoal, to a red heat, carbonic oxide gas and zinc fumes escape. By igniting the oxide in a strong and rapid current of hydrogen gas, metallic zinc is produced; whilst by igniting it in a feeble current of hydrogen gas, crystallized oxide of zinc is obtained (*St. Claire Deville*). Oxide of zinc is insoluble in water. Placed on moist turmeric paper, it does not change the color to brown. In acids, oxide of zinc dissolves readily, and without evolution of gas. When oxide of zinc is heated to redness with chloride of ammonium, fused chloride of zinc is produced, which volatilizes with very great difficulty, if the air is excluded; but readily and completely, with free access of air, and with chloride of ammonium fumes (*H. Rose*).

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* That is to say, complete within the limits indicated just now, so that sulphide of ammonium occasions no turbidity in the filtrate, although it may produce subsequently and after long standing some slight and almost imponderable flakes of sulphide of zinc.

COMPOSITION.

$$\begin{array}{lllll} Zn & = 406{\cdot}59 & = 32{\cdot}53 & = & 80{\cdot}26 \\ O & = 100{\cdot}00 & = 8{\cdot}00 & = & 19{\cdot}74 \\ \hline & 506{\cdot}59 & = 40{\cdot}53 & = & 100{\cdot}00 \end{array}$$

c. Sulphide of zinc, recently precipitated, is a white, loose mass ($Zn\,S, H\,O$), insoluble in water, in caustic alkalies, alkaline carbonates, and alkaline sulphides. It dissolves readily and completely in hydrochloric acid and in nitric acid, but only very sparingly in acetic acid. When dried, the precipitated sulphide of zinc is a white powder; at 212° F. it loses half, and at a red heat the whole of its water. During the latter process some sulphuretted hydrogen escapes, and the remaining sulphide of zinc contains an admixture of oxide of zinc. By roasting in the air, and intense ignition of the residue, small quantities of sulphide of zinc may be readily converted into the oxide.

§ 78.

2. PROTOXIDE OF MANGANESE.

Manganese is weighed either as PROTOSESQUIOXIDE OF MANGANESE (red oxide of manganese)—$Mn\,O + Mn_2O_3) = Mn_3O_4$—or as SULPHATE OF PROTOXIDE OF MANGANESE. For the purpose of converting it into the first form, it is precipitated as CARBONATE OF PROTOXIDE OF MANGANESE, HYDRATED PROTOXIDE OF MANGANESE, BINOXIDE OF MANGANESE, or SULPHIDE OF MANGANESE.

a. Carbonate of protoxide of manganese, recently precipitated, is a white, flocculent mass, nearly insoluble in pure water, but somewhat more soluble in water impregnated with carbonic acid. Presence of carbonate of soda or potassa does not increase its solubility. Recently precipitated carbonate of protoxide of manganese dissolves pretty readily in solution of chloride of ammonium; it is owing to this property that a solution of protoxide of manganese cannot be completely precipitated by carbonate of potassa or soda, in presence of chloride of ammonium (or some other ammoniacal salt), until the latter is completely decomposed. If the precipitate, while still moist, is exposed to the air, or washed with water impregnated with air, it slowly assumes a dirty brownish-white color, part of it becoming converted into hydrated protosesquioxide of manganese. If the precipitate is dried removed from the contact of air, it forms a delicate white powder, persistent in the air [$2\,(Mn\,O, C\,O_2) + aq.$]; but when dried with free access of air, the powder is of a more or less dirty white color. When heated to redness, with access of air, this powder first turns black, and changes subsequently to brown protosesquioxide of manganese. However, this conversion takes some time, and must never be held to be completed until two weighings, between which the precipitate has been ignited again with free access of air, give perfectly corresponding results.

b. Hydrated protoxide of manganese, recently thrown down, forms a white, flocculent precipitate, insoluble in water and in the alkalies, but soluble in chloride of ammonium; this precipitate immediately absorbs oxygen from the air, and turns brown, owing to the formation of hydrated protosesquioxide of manganese. On drying it in the air, a brown powder (hydrated protosesquioxide of manganese) is obtained which, when heated to intense redness, with free access of air, is converted into protosesquioxide of manganese.

c. Protosesquioxide of manganese[*] (red oxide of manganese), artificially produced, is a reddish-brown powder. When exposed to the action of heat, it assumes a black tint, but its weight remains unaltered. It is insoluble in water, and does not alter vegetable colors. Heated to redness with chloride of ammonium, it is converted into protochloride of manganese ($Mn_3O_4 + 4\,H\,Cl = 3\,Mn\,Cl + Cl + 4\,H\,O$).

COMPOSITION.

$$\begin{array}{lllll} 3\,Mn & = 1034{\cdot}05 = & 82{\cdot}71 = & 72{\cdot}10 \\ 4\,O & = 400{\cdot}00 = & 32{\cdot}00 = & 27{\cdot}90 \\ \hline & \,1434{\cdot}05 = & 114{\cdot}71 = & 100{\cdot}00 \end{array}$$

d. Binoxide of manganese is often produced in analysis by exposing a concentrated solution of nitrate of protoxide of manganese to a gradually increased temperature. At 284° F., brown flakes separate, at 311° F. much nitrous acid is disengaged, and the manganese separates as anhydrous binoxide. It is brownish black, and is deposited on the sides of the vessel, with metallic lustre. It is insoluble in weak nitric acid, but dissolves to a small amount in hot and concentrated nitric acid (*Deville*). In hydrochloric acid it dissolves with evolution of chlorine, in concentrated sulphuric acid with evolution of oxygen.

e. Sulphide of manganese, prepared in the humid way, forms a flesh-colored precipitate. From dilute neutral solution, and when precipitated by a limited quantity of sulphide of ammonium, it separates very slowly; much more readily in presence of chloride of ammonium, or of an excess of sulphide of ammonium. Excess of ammonia must be guarded against in the process of precipitation; otherwise some manganese is likely to remain in solution: the precipitation must be effected with yellow sulphide of ammonium, and not with the colorless compound, as the latter would dissolve traces of the precipitate. Presence of chloride of ammonium does not increase its solubility. In dilute acids (hydrochloric acid, sulphuric acid, acetic acid, &c.) it dissolves with evolution of sulphuretted hydrogen. If the precipitate, while still moist, is exposed to the air, or washed with water impregnated with air, its fleshy tint changes to brown, hydrated protosesquioxide of manganese being formed, together with a small portion of sulphate of protoxide of manganese. To guard against this, some yellow sulphide of ammonium must be added to the washing water.

f. Anhydrous sulphate of protoxide of manganese, produced by exposing the crystallized salt to the action of heat, is a white, friable mass, readily soluble in water. It resists the protracted application of a faint red heat; but upon exposure to a more intense red heat, it suffers more or less complete decomposition — oxygen, sulphurous acid, and anhydrous sulphuric acid being evolved, and red oxide of manganese remaining behind.

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[*] All the oxides of manganese finally change to the red oxide, upon ignition with free access of air.

COMPOSITION.

$$\begin{array}{llll} MnO & = 444{\cdot}68 = & 35{\cdot}57 = & 47{\cdot}07 \\ SO_3 & = 500{\cdot}00 = & 40{\cdot}00 = & 52{\cdot}93 \\ \hline & \, 944{\cdot}68 = & 75{\cdot}57 = & 100{\cdot}00 \end{array}$$

§ 79.

3. PROTOXIDE OF NICKEL.

Nickel is precipitated as HYDRATED PROTOXIDE OF NICKEL, and as SULPHIDE OF NICKEL. It is always weighed in the form of PROTOXIDE.

a. Hydrated protoxide of nickel forms an apple-green precipitate, almost absolutely insoluble in water, but soluble in solutions of ammonia and of carbonate of ammonia. From these solutions it is completely precipitated again by potassa or soda, added in excess; application of heat promotes the precipitation. It is unalterable in the air; exposure to a red heat converts it into protoxide of nickel.

b. Protoxide of nickel is a dirty grayish-green powder, insoluble in water, but readily soluble in hydrochloric acid. It does not affect vegetable colors. It suffers no variation of weight upon ignition with free access of air. Mixed with chloride of ammonium and exposed to a red heat, it is reduced to metallic nickel (*H. Rose*); it is also easily reduced by ignition in hydrogen or carbonic oxide gas.

COMPOSITION.

$$\begin{array}{llll} Ni & = 362{\cdot}50 = & 29 = & 78{\cdot}38 \\ O & = 100{\cdot}00 = & 8 = & 21{\cdot}62 \\ \hline & \, 462{\cdot}50 = & 37 = & 100{\cdot}00 \end{array}$$

c. Hydrated sulphide of nickel, prepared in the humid way, forms a black precipitate, insoluble in water. It is insoluble in an excess of sulphide of ammonium perfectly saturated with sulphuretted hydrogen, but it is slightly soluble in ammonia, and still more so in ammonia not fully saturated with sulphuretted hydrogen. When these solutions, which are of a more or less brown color, are exposed to the air, the sulphide of nickel precipitates gradually (see Experiments sub. No. 42). If sulphide of nickel, in a moist state, is exposed to the air, it oxidizes slowly, and is converted into sulphate of protoxide of nickel. It is very sparingly soluble in acetic acid, but somewhat more so in hydrochloric acid. It is more readily soluble still in nitric acid, and most so in nitrohydrochloric acid. It loses its water upon the application of a red heat; when ignited in the air, it is transformed into a basic compound of sesquioxide of nickel with sulphuric acid.

§ 80.

4. PROTOXIDE OF COBALT.

Cobalt is weighed in the PURE METALLIC state; or as PROTOSESQUI-

OXIDE OF COBALT, or as SULPHATE OF PROTOXIDE OF COBALT, or as NITRITE OF SESQUIOXIDE OF COBALT AND POTASSA. Besides the properties of these substances, we have to study here also those of HYDRATED PROTOXIDE OF COBALT, and of SULPHIDE OF COBALT.

a. Hydrated Protoxide of Cobalt.—Upon precipitating a solution of protoxide of cobalt with potassa, a blue precipitate (a basic salt) is formed at first, which, upon boiling with potassa in excess, excluded from contact of air, changes to light red hydrated protoxide of cobalt; if, on the contrary, this process is conducted with free access of air, the precipitate becomes discolored, part of the hydrated protoxide being converted into hydrated sesquioxide. But the hydrated protoxide of cobalt, prepared in this way, retains always a certain quantity of the acid, and, even after the most thorough washing with hot water, also a considerable amount of the alkaline precipitant (*Fremy*, "J. pr. Chem." 57, 81). The results of my own experiments fully confirm this statement of Fremy (Experiment No. 43). The metallic cobalt, therefore, which we obtain upon the ignition of the precipitate in hydrogen gas, manifests a strong alkaline reaction when placed on moist turmeric paper. On account of this unavoidable alkaline admixture, the oxide or metal obtained in this way is unfit for the quantitative estimation of cobalt.

Hydrated protoxide of cobalt is insoluble in water, and also in potassa; it dissolves in solutions of ammoniacal salts; when dried in the air, it absorbs oxygen, and acquires a brownish color.

b. When pure chloride of cobalt or nitrate of protoxide of cobalt is heated to redness in a current of hydrogen gas, pure *metallic cobalt* is obtained, in the form of a grayish-black metallic powder, which is attracted by the magnet, and is more difficultly fusible than gold. If the reduction has been effected at a faint heat, the finely divided metal oxidises in the air to protosesquioxide of cobalt, which is not the case if the reduction has been effected at an intense red heat. Cobalt does not decompose water, neither at the common temperature, nor upon ebullition—except sulphuric acid be present, in which case decomposition will ensue. Heated with concentrated sulphuric acid, it forms sulphate of protoxide of cobalt, with evolution of sulphurous acid. In nitric acid it dissolves readily to nitrate of protoxide of cobalt.

c. Upon ignition of the nitrate of protoxide of cobalt, a black residue is left of constant composition; this residue consists of protosesquioxide of cobalt, a compound corresponding to the protosesquioxide of iron, and which, accordingly, has the formula $Co\,O + Co_2O_3$, or Co_3O_4 (*Rammelsberg, Fremy*). This oxide is insoluble in water; in warm hydrochloric acid it dissolves to protochloride of cobalt, with evolution of chlorine. When heated to redness with chloride of ammonium, it suffers reduction to metallic cobalt. If the ignition is effected with free access of air, or in a current of oxygen, the protochloride, which forms at first, is reconverted partly into amorphous, partly into crystalline protosesquioxide, Co_3O_4 (*Ph. Schwarzenberg*, "Annal. de Chem. u. Pharm." 97, 211), which is insoluble in hydrochloric acid, but dissolves in concentrated sulphuric acid.

COMPOSITION.

$$\begin{array}{lrrr} Co_3 = & 1125 = & 90 = & 73{\cdot}77 \\ O_4 = & 400 = & 32 = & 26{\cdot}23 \\ \hline & 1525 = & 122 = & 100{\cdot}00 \end{array}$$

d. Sulphide of cobalt, produced in the humid way, forms a black precipitate, insoluble in water, in alkalies, and in alkaline sulphides. It is but sparingly soluble in acetic acid and in dilute mineral acids, but more readily so in concentrated mineral acids, and most readily in warm nitrohydrochloric acid. When sulphide of cobalt, in a moist state, is exposed to the air, it slowly absorbs oxygen, and is converted into sulphate of protoxide of cobalt.

e. Sulphate of protoxide of cobalt crystallizes, in combination with 7 aq., slowly in oblique rhombic prisms of a fine red color. The crystals yield the whole of the 7 equivalents of water, at a moderate heat, and are converted into a rose-colored anhydrous salt, which bears the application of a gentle red heat without losing acid. It dissolves rather difficultly in cold, but more readily in hot water. Ignition in a current of hydrogen gas fails to effect its reduction.

COMPOSITION.

$$\begin{aligned} CoO &= 475 = 38 = 48{\cdot}72 \\ SO_3 &= 500 = 40 = 51{\cdot}28 \\ \hline & \ 975 = 78 = 100{\cdot}00 \end{aligned}$$

f. Nitrite of sesquioxide of cobalt and potassa, which is easily produced by mixing a solution of protoxide of cobalt with nitrite of potassa and some nitric or acetic acid, forms a crystalline precipitate of a fine yellow color, which dissolves to a very perceptible amount in pure water, and still more copiously in water containing chloride of sodium and chloride of ammonium. In rather concentrated solutions of salts of potassa ($KO, SO_3, - KCl, - KO, NO_5, - KO, \bar{A}$), on the other hand, it is insoluble even upon boiling. The presence of a *small* proportion of free acetic acid exercises no solvent action under these circumstances. The precipitate does not dissolve in alcohol of 80 per cent.; but it dissolves, though not copiously, in boiling water, to a red fluid. Nitrite of sesquioxide of cobalt and potassa is decomposed with difficulty by solution of potassa, but readily by solution of soda, or by baryta-water; the decomposition is attended with separation of brown hydrated sesquioxide of cobalt (*A. Stromeyer*, "Annal. d. Chem. u. Pharm.," 96, 218). According to this chemist, nitrite of sesquioxide of cobalt and potassa dried at 212° F., has the following composition:

$$\begin{aligned} Co_2O_3 &= 1050{\cdot}00 = 84{\cdot}00 = 19{\cdot}38 \\ 3\,KO &= 1766{\cdot}58 = 141{\cdot}33 = 32{\cdot}61 \\ 5\,NO_3 &= 2375{\cdot}00 = 190{\cdot}00 = 43\ 85 \\ 2\,HO &= 225{\cdot}00 = 18{\cdot}00 = 4{\cdot}16 \\ \hline & \ 5416{\cdot}58 = 433{\cdot}33 = 100{\cdot}00 \end{aligned}$$

100 parts of the compound contain accordingly 17·54 of protoxide of cobalt (CoO), or 13·84 of cobalt. It is decomposed by ignition, and gives protosesquioxide of cobalt and potassa.

§ 81.

5. PROTOXIDE OF IRON; and 6. SESQUIOXIDE OF IRON.

Iron is always weighed in the form of SESQUIOXIDE. Besides the sesquioxide, we have to study the HYDRATED SESQUIOXIDE OF IRON,

SULPHIDE OF IRON, SUCCINATE OF SESQUIOXIDE OF IRON, and ACETATE OF SESQUIOXIDE OF IRON.

a. Hydrated sesquioxide of iron, recently prepared, is a reddish-brown precipitate, insoluble in water, in the alkalies, and in ammoniacal salts, but readily soluble in acids; the process of drying very greatly reduces the bulk of this precipitate. When dry, it presents the appearance of a brown, hard mass, the fracture of which exhibits a shining appearance. If the precipitant alkali is not used in excess, the precipitate contains basic salt; on the other hand, if the alkali has been used in excess, a portion of it is invariably carried down in combination with the sesquioxide of iron,—on which account ammonia alone can properly be used in analysis, as a precipitant for salts of sesquioxide of iron. Perfect washing of larger quantities of the precipitate is effected only with difficulty. According to *v. Kobell* ("Journ. f. prakt. Chem." 62, 98), the labor may be shortened by gently igniting the half-washed precipitate, then triturating the ignited mass with water, and finally completing the operation of washing. Under certain circumstances, for instance by protracted heating of a solution of acetate of sesquioxide of iron on the water-bath (which turns the solution from blood-red to brick-red, and makes it appear turbid by reflected light), and subsequent addition of some sulphuric acid or salt of an alkali, a reddish-brown hydrate is produced, which is insoluble in cold acids, even though concentrated, and is not attacked even by boiling nitric acid (*L. Pean de St. Gilles*, "Journ. f. prakt. Chem." 66, 137).

b. The hydrated sesquioxide of iron is, upon ignition, converted into the *anhydrous sesquioxide*. If the hydrated sesquioxide has not been most carefully and thoroughly dried, the small solid lumps, though dry outside, retain still a portion of water confined within, the sudden conversion of that water into steam, upon the application of a red heat, will cause particles of the sesquioxide to fly about, and may thus lead to loss of substance. Pure sesquioxide of iron, when placed upon moist reddened litmus paper, does not change the color to blue. It dissolves slowly in dilute, but more rapidly in concentrated hydrochloric acid; the application of a moderate degree of heat effects this solution more readily than boiling.

The weight of the sesquioxide does not vary upon ignition in the air; when ignited together with chloride of ammonium, sesquichloride of iron escapes. Ignition with charcoal, protected from access of air, reduces it more or less.

COMPOSITION.

2 Fe	= 700·00	= 56	=	70·00
3 O	= 300·00	= 24	=	30·00
	1000·00	= 80	=	100·00

c. Sulphide of iron, produced in the humid way, forms a black precipitate, slightly soluble in aërated water (with decomposition), insoluble in water containing alkaline sulphides, but readily soluble in mineral acids, both concentrated and dilute. When precipitated from highly dilute solutions, it remains suspended a long time, imparting a blackish-green tint to the fluid; it subsides, however, always completely after the lapse of some time, more especially if the sulphide of ammonium used as precipitant was slightly yellow. When moistened and exposed to the air, hydrated sulphide of iron absorbs oxygen, and acquires a brown tint, hydrated sesquioxide of iron, sulphur, and sulphate of protoxide of iron being formed.

d. When a neutral solution of a salt of sesquioxide of iron is mixed with a neutral solution of an alkaline succinate, a cinnamon-colored precipitate of a brighter or darker tint is formed; this is *succinate of sesquioxide of iron* ($Fe_2O_3, \overline{S}_2$). It results from the nature of this precipitate, that its formation must set free an equivalent of acid (of succinic acid, if the succinate of ammonia is used in excess); *e.g.*, $Fe_2O_3, 3\,S\,O_3 + 3\,N\,H_4O, \overline{S} = Fe_2O_3, \overline{S}_2 + 3\,N\,H_4O, S\,O_3 + \overline{S}$. The free succinic acid does not exercise any perceptible solvent action upon the precipitate in a cold and highly dilute solution, but it redissolves the precipitate a little more readily in a warm solution. The precipitate must therefore be filtered cold, if we want to guard against re-solution. Formerly the precipitate was erroneously supposed to consist of a neutral salt, decomposable by hot water into an insoluble basic and soluble acid compound. Succinate of sesquioxide of iron is insoluble in cold, and but sparingly soluble in hot water. It dissolves readily in mineral acids. Ammonia deprives it of the greater portion of its acid, leaving compounds similar to the hydrated sesquioxide of iron, and which contain from nine to fifteen equivalents of sesquioxide of iron to one equivalent of succinic acid (*Döpping*). Warm ammonia withdraws the acid more completely than cold ammonia.

e. If a solution of pure *acetate of sesquioxide of iron* is heated, it suffers the alteration indicated in *a*, and is afterwards completely precipitated by neutral salts of the alkalies; but if a solution of sesquioxide of iron, containing but little free acid, is mixed with an excess of acetate of soda, and the mixture boiled, a precipitate is produced which contains the whole of the iron present, and consists of a mixture of basic acetate of sesquioxide of iron with the reddish-brown hydrate mentioned in *a*.

BASES OF THE FIFTH GROUP.

§ 82.

1. Oxide of Silver.

Silver may be weighed in the METALLIC state, or as CHLORIDE OF SILVER, SULPHIDE OF SILVER, and CYANIDE OF SILVER.

a. Metallic silver, obtained by the ignition of salts of silver with organic acids, &c., is a loose, light, white, glittering mass of metallic lustre; but, when obtained by reducing chloride of silver, &c., in the humid way, by the agency of zinc, it is a dull gray powder. It is not fusible over a Berzelius' lamp. Ignition leaves its weight unaltered. It dissolves readily and completely in dilute nitric acid.

b. Chloride of silver, recently precipitated, is a white, curdy mass, which, upon drying, assumes a pulverulent character. It is wholly insoluble in water, and in nitric acid, and but very sparingly soluble in concentrated hydrochloric acid, from which solution it is almost completely thrown down again on the addition of water. It is not, or only very slightly, attacked by sulphuric acid, even though concentrated. It is slightly soluble in solutions (more particularly when concentrated), of chloride of ammonium (but of no other ammoniacal salt), chloride of sodium, and chloride of potassium. It dissolves pretty copiously in solution of nitrate of oxide of mercury, from which solution it is precipitated again by alkaline acetates. It dissolves readily in caustic ammonia. Exposed to the light, it speedily acquires, first a violet, finally a black tint, owing to the escape of chlorine, and the conversion of the salt to Ag_2Cl. This modification of the chloride of silver is, however, so very superficial only, that it fails to show the loss of chlorine, even by a very delicate balance. When heated, chloride of silver acquires a yellow tint; at 500° F., it fuses to a transparent, yellow liquid, which, after cooling, presents the appearance of a colorless or slightly yellowish mass. Exposed to a very intense degree of red heat, chloride of silver volatilizes unaltered. When fused in a current of chlorine gas, it absorbs a little of the latter, but yields it again completely upon cooling. Ignition with charcoal fails to effect its reduction to the metallic state; but it may be readily reduced to metallic silver, by igniting it in a current of hydrogen or carbonic oxide gas.

COMPOSITION.

$$\begin{array}{lrrr} Ag = & 1349{\cdot}66 = & 107{\cdot}97 = & 75{\cdot}28 \\ Cl = & 443{\cdot}28 = & 35{\cdot}46 = & 24{\cdot}72 \\ \hline & 1792{\cdot}94 = & 143{\cdot}43 = & 100{\cdot}00 \end{array}$$

c. *Sulphide of silver*, prepared in the humid way, is a black precipitate, insoluble in water, dilute acids, alkalies, and alkaline sulphides. This precipitate is unalterable in the air, and may be dried at 212° F., without suffering decomposition. It dissolves in concentrated nitric acid, with separation of sulphur. Solution of cyanide of potassium fails to dissolve sulphide of silver, except the cyanide be used greatly in excess; but the sulphide separates readily again, even upon the addition of water (*Bechamp*, "Journ. f. prakt. Chem." 60, 64.)

COMPOSITION.

$$\begin{array}{lrrr} Ag = & 1349{\cdot}66 = & 107{\cdot}97 = & 87{\cdot}07 \\ S = & 200{\cdot}00 = & 16{\cdot}00 = & 12{\cdot}93 \\ \hline & 1549{\cdot}66 = & 123{\cdot}97 = & 100{\cdot}00 \end{array}$$

d. *Cyanide of silver*, recently precipitated, forms a white curdy mass insoluble in water and dilute nitric acid, soluble in cyanide of potassium and also in ammonia; exposure to light fails to impart the slightest tinge of black to it; it may be dried at 212° F., without suffering decomposition. Upon ignition, it is decomposed into cyanogen gas, which escapes, and metallic silver, which remains, mixed with a little paracyanide of silver. By boiling with a mixture of equal parts of sulphuric acid and water, it is, according to *Glassford* and *Napier*, converted into sulphate of silver, with liberation of hydrocyanic acid.

COMPOSITION.

$$\begin{array}{lrrr} Ag = & 1349{\cdot}66 = & 107{\cdot}97 = & 80{\cdot}60 \\ C_2N = & 325{\cdot}06 = & 26{\cdot}00 = & 19{\cdot}40 \\ \hline & 1674{\cdot}72 = & 133{\cdot}97 = & 100{\cdot}00 \end{array}$$

§ 83.

2. Oxide of Lead.

Lead is weighed as OXIDE, SULPHATE, CHROMATE, CHLORIDE, and SULPHIDE OF LEAD. Besides these compounds, we have also to study the CARBONATE and the OXALATE OF LEAD.

a. Neutral carbonate of lead forms a heavy, white, pulverulent precipitate. It is but very slightly soluble in perfectly pure (boiled) water (one part requiring 50550 parts of pure water (see Experiment No. 44, *a*); but it dissolves somewhat more readily in water containing ammonia and ammoniacal salts (comp. Experiments No. 44, *b* and *c*). It dissolves also somewhat more readily in water impregnated with carbonic acid, than in pure water. It loses its carbonic acid when ignited.

b. Oxalate of lead is a white powder, very sparingly soluble in water. The presence of ammonia salts slightly increases its solubility (Experiment No. 45). When heated in close vessels, it leaves suboxide of lead; but when heated, with access of air, yellow oxide (protoxide).

c. Oxide, or *protoxide, of lead*, produced by igniting the carbonate or oxalate, is a lemon-yellow powder, inclining sometimes to a reddish yellow, or to a pale yellow. When this yellow oxide of lead is heated, it assumes a brownish-red color, without the slightest variation of weight. It fuses at an intense red heat. Ignition with charcoal reduces it. When exposed to a white heat, it rises in vapor. Placed upon moist reddened litmus-paper, it changes the color to blue. When exposed to the air, it slowly absorbs carbonic acid. Mixed with chloride of ammonium and ignited, it is converted into chloride of lead. Oxide of lead in a state of fusion readily dissolves silicic acid and the earthy bases with which the latter is combined.

COMPOSITION.

$$\begin{array}{lrrr} Pb = & 1294{\cdot}64 = & 103{\cdot}57 = & 92{\cdot}83 \\ O \;= & 100{\cdot}00 = & 8{\cdot}00 = & 7{\cdot}17 \\ \hline & 1394{\cdot}64 = & 111{\cdot}57 = & 100{\cdot}00 \end{array}$$

d. Sulphate of lead is a heavy white powder. It dissolves, at the common temperature, in 22800 parts of pure water (Experiment No. 46); it is less soluble still in water containing sulphuric acid (one part requiring 36500 parts—Experiment No. 47); it is far more readily soluble in water containing ammoniacal salts; from this solution it may be precipitated again by adding sulphuric acid in excess (Experiment No. 48). It is almost entirely insoluble in alcohol and spirit of wine. Of the salts of ammonia, the nitrate, acetate, and tartrate are more especially suited to serve as solvents for sulphate of lead; the two latter salts of ammonia are made strongly alkaline by addition of ammonia, previous to use (*Wackenroder*). Sulphate of lead dissolves in concentrated hydrochloric acid, upon heating. In nitric acid it dissolves the more readily, the more concentrated and hotter the acid; water fails to precipitate it from its solution in nitric acid; but the addition of a copious amount of dilute sulphuric acid causes its precipitation from this solution. The more nitric acid the solution contains, the more sulphuric acid is required to throw down the sulphate of lead. Sulphate of lead dissolves sparingly in concentrated sulphuric acid, and the dissolved portion precipitates again upon diluting the acid with water (and more completely still, upon addition of alcohol). The solutions of carbonates and bi-carbonates of the alkalies convert sulphate of lead, even at the common temperature, completely into carbonate of lead. The solutions of the carbonates, but not those of the bi-carbonates, dissolve some oxide of lead in this process (*H. Rose*, "Pogg. Annal." 95, 426). Sulphate of lead dissolves readily in hot solutions of potassa or soda. It is unalterable in the air, and at a gentle red heat; when exposed to a higher degree of heat, it fuses without suffering decomposition (Experiment No. 49), provided always the action of reducing gases be completely excluded—for, if this is not the case, the weight will continually diminish, owing to the ensuing reduction of $Pb\,O, S\,O_3$ to $Pb\,S$ (*Erdmann*, "Journ. f. prakt. Chem.," 62, 381). When sulphate of lead is ignited with charcoal, sulphide of lead is formed at first, the sulphur reducing in its turn the sulphuric acid of an undecomposed portion of the sulphate to sulphurous acid, giving thus, on both sides, rise to the separation of metallic lead. Fusion with cyanide of potassium reduces the whole of the lead to the metallic state.

COMPOSITION.

$$\begin{array}{rcrcrcr} Pb\,O & = & 1394{\cdot}64 & = & 111{\cdot}57 & = & 73{\cdot}56 \\ S\,O_3 & = & 500{\cdot}00 & & 40{\cdot}00 & = & 26{\cdot}44 \\ \hline & & 1894{\cdot}64 & = & 151{\cdot}57 & = & 100{\cdot}00 \end{array}$$

e. Chloride of lead exists either in the form of small, brilliant crystalline needles, or as a white powder; it dissolves, at the common temperature, in 135 parts of water; and is still more soluble in hot water. It dissolves less readily in water mixed with hydrochloric or nitric acid, one part requiring 1636 parts of water containing nitric acid (*Bischof*); it dissolves freely in concentrated hydrochloric acid, from which solution it may be precipitated again by addition of water. It is extremely sparingly soluble in spirit of wine of from 70 to 80 per cent., and altogether insoluble in absolute alcohol. It is unalterable in the air. It fuses at a temperature below red heat, without suffering any diminution of weight. When exposed to a higher temperature, with access of air, it volatilizes slowly, being partially decomposed: chlorine gas escapes, and a mixture of oxide and chloride of lead remains.

COMPOSITION.

$$\begin{array}{rcrcrcr} Pb & = & 1294{\cdot}64 & = & 103{\cdot}57 & = & 74{\cdot}49 \\ Cl & = & 443{\cdot}28 & = & 35{\cdot}46 & = & 25{\cdot}51 \\ \hline & & 1737{\cdot}92 & = & 139{\cdot}03 & = & 100{\cdot}00 \end{array}$$

f. Sulphide of lead, prepared in the humid way, is a black precipitate, insoluble in water, dilute acids, alkalies, and alkaline sulphides. This precipitate is unalterable in the air, and may be dried at 212° F., without suffering decomposition. It dissolves in concentrated hot hydrochloric acid, with evolution of sulphuretted hydrogen. In moderately concentrated nitric acid, sulphide of lead dissolves, upon the application of heat, with separation of sulphur;—if the acid is rather concentrated, a small portion of sulphate of lead is also formed. Fuming nitric acid acts energetically upon sulphide of lead, and converts it into sulphate of lead, without separation of sulphur (Experiment No. 50).

COMPOSITION.

$$\begin{array}{lllll} Pb = & 1294{\cdot}64 = & 103{\cdot}57 = & 86{\cdot}61 \\ S = & 200{\cdot}00 = & 16{\cdot}00 = & 13{\cdot}39 \\ \hline & 1494{\cdot}64 = & 119{\cdot}57 = & 100{\cdot}00 \end{array}$$

g. For the composition and properties of *chromate of lead*, see *chromic acid*, § 93.

§ 84.

3. SUBOXIDE OF MERCURY; and 4. OXIDE OF MERCURY.

Mercury is weighed either in the METALLIC state, as SUBCHLORIDE, or as SULPHIDE OF MERCURY, or occasionally also as OXIDE.

a. Metallic mercury is liquid at the common temperature; it has a tin-white color. When pure, it presents a perfectly bright surface. It is unalterable in the air at the common temperature. It boils at 680° F. and is perceptibly volatile even between 68° and 80° F.; at this temperature it volatilizes, however, very slowly. Upon long-continued boiling with water, a small portion of mercury volatilizes, and traces escape along with the aqueous vapor, whilst a very minute proportion remains suspended in the water (comp. Experiment No. 51). This suspended portion of mercury subsides completely after long standing. When metallic mercury is precipitated from a fluid, in a very minutely divided state, the small globules will readily unite into a large one if the mercury be perfectly pure; but even the slightest trace of extraneous matter, such as fat, &c., adhering to the mercury will prevent the union of the globules. Mercury does not dissolve in hydrochloric acid, not even in concentrated; it is barely soluble in dilute cold sulphuric acid, but dissolves readily in nitric acid, and in boiling concentrated sulphuric acid.

b. Subchloride of mercury, prepared in the humid way, is a heavy white powder. It is almost absolutely insoluble in cold water; in boiling water it is gradually decomposed into chlorine and mercury; upon continued boiling, the residue acquires a gray color. Highly dilute hydrochloric acid fails to dissolve subchloride of mercury at the common temperature, but dissolves it slowly at a higher temperature; upon ebullition, with access of air, the whole of the subchloride is gradually dissolved by the dilute acid: the solution contains chloride of mercury ($Hg_2Cl + H\,Cl + O = 2\,Hg\,Cl + H\,O$). Subchloride of mercury, when acted upon by boiling concentrated hydrochloric acid, is rather speedily decomposed into mercury, which remains undissolved, and chloride of mercury, which dissolves in the menstruum. Boiling nitric acid dissolves subchloride of mercury, and converts it into chloride and nitrate of mercury. Chlorine water and nitrohydrochloric acid dissolve it to chloride, even in the cold. Solutions of chloride of ammonium, chloride of sodium, and chloride of potassium, decompose subchloride of mercury into metallic mercury and chloride of mercury, which latter dissolves in the menstruum; at a low temperature, this decomposition is confined to a small portion of the subchloride, but the application of heat promotes the decomposing action of the alkaline solutions. Subchloride of mercury does not affect vegetable colors; it is unalterable in the air, and may be dried at 212° F., without suffering any diminution of weight; when exposed to a higher degree of heat, though still below redness, it volatilizes completely, without previous fusion.

COMPOSITION.

$$\begin{array}{lrrr} 2\,Hg = & 2501\cdot20 = & 200\cdot10 = & 84\cdot95 \\ Cl & 443\cdot28 = & 35\cdot46 = & 15\cdot05 \\ \hline & 2944\cdot48 = & 235\cdot56 = & 100\cdot00 \end{array}$$

c. Sulphide of mercury, prepared in the humid way, is a black powder, insoluble in water. Dilute hydrochloric acid and dilute nitric acid fail to dissolve it, and it remains insoluble even in boiling hydrochloric acid; it is only very slightly soluble in hot concentrated nitric acid, but it dissolves readily in nitrohydrochloric acid. In solution of potassa it is insoluble, even on boiling; but it dissolves readily in sulphide of potassium, though only in presence of free alkali (Experiment No. 52). Sulphide of ammonium and cyanide of potassium fail to dissolve it. In the air it is unalterable, even in the moist state, and at 212° F. When exposed to a higher temperature, it sublimes completely and unaltered.

COMPOSITION.

$$\begin{array}{lrrr} Hg = & 1250\cdot6 = & 100\cdot05 = & 86\cdot21 \\ S\ = & 200\cdot0 = & 16\cdot00 = & 13\cdot79 \\ \hline & 1450\cdot6 = & 116\cdot05 = & 100\cdot00 \end{array}$$

d. Oxide of mercury is a crystalline brick-colored powder, which, when exposed to the action of heat, changes to the color of cinnabar, and subsequently to a violet-black tint. It bears a tolerably strong heat without suffering decomposition; but, when heated to incipient redness, it is decomposed into mercury and oxygen; perfectly pure oxide of mercury leaves no residue upon continued exposure to a red heat.

COMPOSITION.

$$\begin{array}{lrrr} Hg = & 1250\cdot6 = & 100\cdot05 = & 92\cdot59 \\ O\ = & 100\cdot0 = & 8\cdot00 = & 7\cdot41 \\ \hline & 1350\cdot6 = & 108\cdot05 = & 100\cdot00 \end{array}$$

§ 85.

5. OXIDE OF COPPER.

Copper is usually weighed in the metallic state or in the form of OXIDE, occasionally also as SUBSULPHIDE OF COPPER. Besides these forms, we have to examine SULPHIDE OF COPPER, METALLIC COPPER, SUBOXIDE OF COPPER, and SULPHO-SUBCYANIDE OF COPPER.

a. Copper, in the pure state, is a metal of a peculiar reddish-brown color. It fuses only at a white heat. Exposure to dry air, or to moist air, free from carbonic acid, leaves it unaltered; but upon exposure to moist air impregnated with carbonic acid, it becomes gradually tarnished and coated with a film, first of a blackish gray, finally of a bluish green color. Upon ignition in the air, a layer of black oxide forms on its surface. Hydrochloric acid fails to dissolve it, even upon boiling, if the air is excluded; but with free access of air, it dissolves it slowly. Copper dissolves readily in nitric acid. In ammonia it dissolves slowly if free access is given to the air; but it remains insoluble in that menstruum if the air is excluded. Metallic copper brought into contact with solution of chloride of copper in hydrochloric acid, or with an ammoniacal solution of oxide of copper, reduces the chloride to subchloride, and the black oxide to red oxide (suboxide), an equivalent of metal being dissolved for every equivalent of chloride or oxide.

b. Oxide of Copper.—If a dilute, cold, aqueous solution of a salt of copper is mixed with solution of potassa in excess, a light blue precipitate of hydrated oxide of copper ($Cu\,O, H\,O$) is formed, which it is found difficult to wash. If the precipitate be left in the fluid from which it has been precipitated, it will, even at a temperature of from 68° to 80° F., gradually acquire a brownish-black tint, yielding up the greater part of its water of hydration, and changing to $3\,Cu\,O, H\,O$ (*Harms*, "Arch. der Pharm." 139, 35).

This transformation is immediate upon heating the fluid nearly to boiling. The fluid filtered off from the black precipitate is free from copper. If the solutions in question are mixed in a concentrated state, the fluid, in addition to the formation of the blue precipitate, acquires a blue color, owing to a portion of very minutely divided hydrated oxide remaining suspended in it. From a fluid of this description, even protracted boiling will fail to precipitate all the copper which it contains; after previous dilution with water, however, the desired object is readily attained. If a solution of a salt of copper happens to contain non-volatile organic substances in admixture, potassa in excess will, even upon boiling, fail to precipitate the whole of the copper as oxide. The hydrated oxide of copper ($3\,Cu\,O, H\,O$) precipitated with potassa or soda from hot dilute solutions of salts of copper retains a portion of the precipitant with considerable tenacity; it may, however, be completely freed from this by washing with boiling water. Oxide of copper, prepared by the decomposition of carbonate or nitrate of copper by the action of heat, is a brownish-black, or black powder, the weight of which remains unaltered upon strong ignition over the gas- or spirit-lamp, provided all reducing gases be excluded (Exper. No. 53). The same powder is produced by igniting the oxide of copper obtained by precipitation. But if the oxide of copper, no matter whether prepared in the dry or in the humid way, is exposed to a heat approaching the fusing point of metallic copper, it fuses, yields oxygen, and becomes converted into Cu_8O_5. (*Favre* and *Maumené*.) It is very readily reduced by ignition with charcoal; heated in the air, the reduced metallic copper re-oxidizes. Oxide of copper, in contact with the atmosphere, absorbs water; oxide that has been but slightly ignited, absorbs the water more rapidly than such as has been strongly ignited (Experiment No. 54). Oxide of copper is nearly insoluble in water; but it dissolves readily in hydrochloric acid, nitric acid, &c.; less readily in ammonia. It does not affect vegetable colors.

COMPOSITION.

$$\begin{array}{lcrcrcr} Cu & = & 396{\cdot}00 & = & 31{\cdot}68 & = & 79{\cdot}84 \\ O & = & 100{\cdot}00 & = & 8{\cdot}00 & = & 20{\cdot}16 \\ \hline & & 496{\cdot}00 & = & 39{\cdot}68 & = & 100{\cdot}00 \end{array}$$

c. Sulphide of copper, prepared in the humid way, is a brownish-black, or black precipitate, almost absolutely insoluble in water;* when this precipitate, in a moist state, is exposed to the air, it acquires a greenish tint and the property of reddening litmus paper, and becomes gradually altogether converted into sulphate of copper. Sulphide of copper dissolves readily in boiling nitric acid, with separation of sulphur. Hydrochloric acid dissolves it with difficulty. It does not dissolve in solutions of potassa and of sulphide of potassium, particularly if these solutions be boiling; but it dissolves perceptibly in sulphide of ammonium, and readily in cyanide of potassium. Upon ignition in a current of hydrogen gas it is reduced to Cu_2S.

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* In some experiments made by me on the occasion of my analysis of the springs of Weilbach, I found that about 950000 parts of water are required to dissolve 1 part of $Cu\,S$.

d. If the blue solution which is obtained upon adding to solution of oxide of copper tartaric acid and then solution of soda in excess, is mixed with solution of grape sugar or sugar of milk, and heat applied, there speedily forms an orange-yellow precipitate of hydrated suboxide of copper, which contains the whole of the copper originally present in the solution, and after a short time, more particularly upon the application of a stronger heat, turns red, owing to the conversion of the hydrate into simple suboxide (Cu_2O). The precipitate, which is insoluble in water, retains a portion of alkali with considerable tenacity. When acted upon with dilute sulphuric acid, it gives sulphate of copper, which dissolves in the menstruum, and metallic copper, which separates.

e. Sulpho-subcyanide of copper (Cu_2, $Cy\,S_2$), which is always formed when sulphocyanide of potassium is added to a solution of oxide of copper, mixed with sulphurous or hypophosphorous acid, is a white precipitate insoluble in water, as well as in dilute hydrochloric or sulphuric acid. Dried at 239° F., the salt retains still from 1 to 3 per cent. of water, which is driven off only by heating to incipient decomposition; sulpho-subcyanide of copper is, therefore, not well adapted to serve for direct weighing. When fused in conjunction with sulphur, with exclusion of air, it changes to Cu_2S (*Rivot*, "Journ. f. Prak. Chem.," 62, 252). When heated with hydrochloric acid and chlorate of potassa, or with sulphuric acid and nitric acid, it is dissolved and suffers decomposition. Solutions of potassa and soda separate hydrated suboxide of copper, with formation of sulphocyanides of the alkali metal.

f. Subsulphide of copper, produced by heating Cu S in a current of hydrogen gas, or Cu_2, $Cy\,S_2$, with sulphur, is a grayish-black mass, which may be ignited and fused, without suffering decomposition, if the air is excluded.

COMPOSITION.

2 Cu	792 =	63·36 =	79·84
S	200 =	16·00 =	20·16
	992 =	79·36 =	100·00

§ 86.

6. TEROXIDE OF BISMUTH.

Bismuth is weighed in the form of TEROXIDE or as CHROMATE OF TEROXIDE OF BISMUTH ($Bi\,O_3$, $2\,Cr\,O_3$). Besides these compounds, we have to study here the BASIC CARBONATE and the TERSULPHIDE OF BISMUTH.

a. Teroxide of bismuth, prepared by igniting the carbonate or nitrate, is a pale lemon-yellow powder which, under the influence of heat, assumes transiently a dark yellow or reddish-brown tint. When heated to intense redness, it fuses, without alteration of weight. Ignition with charcoal, or in a current of carbonic oxide gas, reduces it to the metallic state. Fusion with cyanide of potassium also effects its complete reduction to the metallic state (*H. Rose*, "Journ. f. Prakt. Chem.," 61, 188). It is insoluble in water, and does not affect vegetable colors. It dissolves readily in those acids which form soluble salts with it. When ignited with chloride of ammonium it gives metallic bismuth, the reduction being attended with deflagration.

COMPOSITION.

$$\begin{array}{lrrr} Bi & = 2599{\cdot}95 = & 208 = & 89{\cdot}655 \\ O_3 & = 300{\cdot}00 = & 24 = & 10{\cdot}345 \\ \hline & 2899{\cdot}95 = & 232 = & 100{\cdot}000 \end{array}$$

b. Carbonate of Teroxide of Bismuth.—Upon adding carbonate of ammonia in excess to a solution of a salt of bismuth, free from hydrochloric acid, a white precipitate of carbonate of bismuth ($Bi\,O_3,C\,O_2$) is immediately formed; part of this precipitate, however, redissolves in the excess of the precipitant. But if the fluid with the precipitate be heated previous to filtration, the filtrate will be perfectly free from any trace of bismuth. Carbonate of potassa likewise precipitates solutions of salts of bismuth completely; but the precipitate in this case invariably contains traces of potassa, which it is very difficult to remove by washing. Carbonate of soda precipitates solutions of salts of bismuth less completely than the carbonates of ammonia and potassa. The precipitate obtained by means of carbonate of ammonia, is easily washed; it is nearly insoluble in water, but dissolves readily, with effervescence, in hydrochloric acid and nitric acid. Upon ignition it loses its carbonic acid, leaving teroxide of bismuth.

c. Chromate of teroxide of bismuth ($Bi\,O_3$, $2\,Cr\,O_3$), which is produced by adding bichromate of potassa, slightly in excess, to a neutral solution of nitrate of teroxide of bismuth, is an orange-yellow, dense, readily subsiding precipitate, insoluble in water, even in presence of some free chromic acid, but soluble in hydrochloric acid and nitric acid. It may be dried at from 212° to 233·6° F., without suffering decomposition (*Löwe*, "Journ. f. Prakt. Chem.," 67, 291).

COMPOSITION.

$$\begin{array}{lrrr} Bi\,O_3 & = 2899{\cdot}95 = & 232{\cdot}0 = & 69{\cdot}59 \\ 2\,Cr\,O_3 & = 1269{\cdot}40 = & 101{\cdot}5 = & 30{\cdot}41 \\ \hline & 4169{\cdot}35 = & 333{\cdot}5 = & 100{\cdot}00 \end{array}$$

d. Tersulphide of bismuth, prepared in the humid way, is a brownish-black, or black precipitate, insoluble in water, dilute acids, alkalies, alkaline sulphides, and cyanide of potassium. In moderately concentrated nitric acid it dissolves, at a high temperature, as a nitrate, with separation of sulphur. It is unalterable in the air, and may be dried at 212° F., without undergoing any change. Fusion with cyanide of potassium completely reduces tersulphide of bismuth to the metallic state (*H. Rose*).

COMPOSITION.

Bi = 2599·95 = 208 = 81·25
3 S = 600·00 = 48 = 18·75

3199·95 = 256 = 100·00

§ 87.

7. Oxide of Cadmium.

Cadmium is weighed either as OXIDE or as SULPHIDE OF CADMIUM. Besides these substances, we have to examine CARBONATE OF CADMIUM.

a. Oxide of cadmium, produced by igniting the carbonate or nitrate of cadmium, is a powder, the color of which varies from yellowish brown to reddish brown. The application of a white heat fails to fuse, volatilize, or decompose it; it is insoluble in water, but dissolves readily in acids; it does not alter vegetable colors. Ignition with charcoal reduces it readily, the metallic cadmium escaping in the form of vapor.

COMPOSITION.

Cd = 696·77 = 55·74 = 87·45
O = 100·00 = 8·00 = 12·55

796·77 = 63·74 = 100·00

b. Carbonate of cadmium is a white precipitate, insoluble in water and in the fixed alkaline carbonates, and extremely sparingly soluble in carbonate of ammonia. It loses its water completely upon desiccation. Ignition converts it into oxide of cadmium.

c. Sulphide of cadmium, produced in the humid way, is a lemon-yellow or orange-yellow precipitate, insoluble in water, dilute acids, alkalies, alkaline sulphides, and cyanide of potassium (Experiment No. 55). It dissolves in concentrated hydrochloric acid, with evolution of sulphuretted hydrogen, and in moderately concentrated hot nitric acid, with separation of sulphur. It may be washed, and dried at 212°, without undergoing decomposition.

COMPOSITION.

Cd = 696·77 = 55·74 = 77·78
S = 200·00 = 16·00 = 22·22

896·77 = 71·74 = 100·00

METALLIC OXIDES OF THE SIXTH GROUP.

§ 88.

1. Teroxide of Gold.

Gold is always weighed in the metallic state. Besides METALLIC GOLD, we have to consider TERSULPHIDE OF GOLD.

a. Metallic gold, obtained by precipitation, presents the appearance of a blackish-brown powder, destitute of metallic lustre, which it assumes, however, upon pressure or friction; when coherent in a compact mass, it exhibits the characteristic bright yellow color peculiar to it. It fuses only at a white heat, and resists, accordingly, all attempts at fusion over a spirit-lamp. It remains wholly unaltered in the air and at a red heat, and is not in the slightest degree affected by water, nor by any simple acid. Nitrohydrochloric acid dissolves it to terchloride.

b. Tersulphide of Gold.—When sulphuretted hydrogen is transmitted through a cold dilute solution of terchloride of gold, the whole of the gold separates as tersulphide ($Au\,S_3$), in form of a brownish-black precipitate. If this precipitate is left in the fluid, it is gradually transformed into metallic gold and free sulphuric acid. Upon transmitting sulphuretted hydrogen through a warm solution of terchloride of gold, a protosulphide ($Au\,S$) precipitates, with simultaneous formation of sulphuric acid and hydrochloric acid.

$$(2\,Au\,Cl_3 + 3\,HS + 3\,HO = 2\,AuS + 6\,HCl + SO_3.)$$

The tesrulphide ($Au\,S_3$) is insoluble in water, hydrochloric acid, and nitric acid, but dissolves in nitrohydrochloric acid. The colorless sulphide of ammonium fails to dissolve it; but it dissolves almost entirely in the yellow sulphide of ammonium, and completely upon addition of potassa. It dissolves in potassa, with separation of gold. Yellow sulphide of potassium dissolves it completely. Exposure to a moderate heat reduces it to the metallic state.

§ 89.

2. BINOXIDE OF PLATINUM.

Platinum is invariably weighed in the METALLIC STATE; it is generally precipitated as BICHLORIDE OF PLATINUM AND CHLORIDE OF AMMONIUM, or as BICHLORIDE OF PLATINUM AND CHLORIDE OF POTASSIUM, rarely as BISULPHIDE OF PLATINUM.

a. Metallic platinum, produced by igniting the bichloride of platinum and chloride of ammonium, or the bichloride of platinum and chloride of potassium, presents the appearance of a gray, lustreless, porous mass (spongy platinum). The fusion of platinum can be effected only at the very highest degrees of heat. It remains wholly unaltered in the air, and even the most intense heat of our furnaces fails to affect it. It is insoluble in water and in any simple acid, and nearly insoluble in aqueous solutions of the alkalies. Nitrohydrochloric acid dissolves it to bichloride.

b. The properties of *bichloride of platinum and chloride of potassium,* and those of *bichloride of platinum and chloride of ammonium,* have been given already in §§ 68 and 70.

c. Bisulphide of Platinum.—When a concentrated solution of bichloride of platinum is mixed with sulphuretted hydrogen water, or when sulphuretted hydrogen gas is transmitted through a more dilute solution of the bichloride, no precipitate forms at first; after standing some time, however, the solution turns brown, and finally a precipitate subsides. But if the mixture of solution of bichloride of platinum with sulphuretted hydrogen in excess, is gradually heated to ebullition, the whole of the platinum separates as bisulphide (free from any admixture of bichloride of platinum). The bisulphide of platinum is insoluble in water and in simple acids; but it dissolves in nitrohydrochloric acid. It dissolves partly in caustic alkalies, with separation of platinum, and completely in alkaline sulphides. When sulphuretted hydrogen is transmitted through water holding minutely divided bisulphide of platinum in mechanical suspension, the bisulphide, absorbing sulphuretted hydrogen, acquires a light grayish-brown color; the sulphuretted hydrogen thus absorbed, separates again upon exposure to the air. When moist bisulphide of platinum is exposed to the air, it is gradually decomposed, being converted into metallic platinum and sulphuric acid, Ignition in the air reduces bisulphide of platinum to the metallic state.

§ 90.

3. TEROXIDE OF ANTIMONY.

Antimony is most generally weighed as TERSULPHIDE OF ANTIMONY, more rarely as ANTIMONIOUS ACID, or in the METALLIC state.

a. Upon transmitting sulphuretted hydrogen through a solution of terchloride of antimony mixed with tartaric acid, an orange-red precipitate of *hydrated tersulphide of antimony* is obtained, mixed at first with a small portion of basic terchloride of antimony. However, if the fluid is thoroughly saturated with sulphuretted hydrogen, and a gentle heat applied, the terchloride of antimony mixed with the precipitate is decomposed, and the pure hydrated tersulphide of antimony obtained; which, subsequently, in the process of drying, loses its water of hydration. Tersulphide of antimony is insoluble in water and dilute acids; it dissolves in concentrated hydrochloric acid, with evolution of sulphuretted hydrogen. Brought into contact with fuming nitric acid and a little hydrochloric acid, it oxidizes with much violence, and is converted into sulphate of teroxide of antimony. It dissolves readily in solutions of potassa, sulphide of ammonium, and sulphide of potassium, but is only sparingly soluble in ammonia. It may be dried at 212° F., without suffering decomposition; when dried at that temperature it is unalterable in the air; but it always retains a little water, which it does not yield, even at 374° F.; at 392° F., however, the water is completely expelled, and the tersulphide acquires a black color and crystalline appearance (*H. Rose,* "Journ. f. prakt. Chem.," 59, 331). When recently precipitated tersulphide of antimony is long boiled with water, it is decomposed and converted into teroxide of antimony, which dissolves in the water, and sulphuretted hydrogen. When tersulphide of antimony is exposed for some time to the air, water being present, it absorbs oxygen, and dissolves gradually as sulphate of teroxide of antimony. The higher sulphides of antimony, corresponding to antimonious and antimonic acid, are likewise insoluble in water; they dissolve, however, sparingly in water impregnated with sulphuretted hydrogen.

COMPOSITION.

$$\begin{array}{lrrr} Sb = & 1503 = & 120{\cdot}2 = & 71{\cdot}47 \\ S_3 = & 600 = & 48{\cdot}0 = & 28{\cdot}53 \\ \hline & 2103 = & 168{\cdot}2 = & 100{\cdot}00 \end{array}$$

b. Antimonious acid is a white powder, which, when heated, acquires transiently a yellow tint; it is infusible; it is fixed, provided reducing gases be excluded.* It is almost insoluble in water, and dissolves in hydrochloric acid with very great difficulty. It undergoes no alteration by the action of sulphide of ammonium. It manifests an acid reaction when placed upon moist litmus paper.

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* As *Berzelius,* at a former period, and *Dexter,* quite lately ("Pogg. Ann.," 100, 563), have, upon the oxidation of antimony by nitric acid, and ignition of the residue, obtained results in contradiction to this statement, some further inquiry into the subject is desirable, the more so, as the equivalent of antimony derived from *Dexter's* experiments differs considerably from that given by *Schneider.*

COMPOSITION.

$$\begin{array}{rcl} \text{Sb} = 1503 = 120{\cdot}2 = & 78{\cdot}98 \\ 4\ \text{O} = \underline{\ 400} = \underline{\ 32{\cdot}0} = & \underline{21{\cdot}02} \\ 1903 = 152{\cdot}2 = & 100{\cdot}00 \end{array}$$

c. Metallic antimony, produced in the humid way, by precipitation, presents the appearance of a lustreless black powder. Metallic antimony is insoluble in water; however, when exposed to the action of air, in presence of water, it oxidizes slowly, and the oxide formed dissolves in the water. The powder of antimony may be dried at 212° F. without suffering any alteration. It fuses at a moderate red heat. Upon ignition in a current of gas, *e. g.* hydrogen gas, it volatilizes, without formation of antimonetted hydrogen. Concentrated hydrochloric acid has very little action on it, even upon ebullition. Nitric acid converts it into teroxide of antimony, mixed with a greater or less proportion of antimonious acid, according to the greater or less degree of concentration of the oxidizing acid.

§ 91.

4. PROTOXIDE OF TIN; and 5. BINOXIDE OF TIN.

Tin is generally weighed in the form of BINOXIDE; besides the binoxide, we have to examine PROTOSULPHIDE and BISULPHIDE OF TIN.

a. Binoxide of Tin (*a* and *b*).—The hydrate of the binoxide *b* (*hydrated metastannic acid*) is obtained in the form of a white precipitate, by the action of nitric acid upon metallic tin, or by evaporating a solution of a salt of tin with nitric acid in excess. This precipitate is insoluble in water, nitric acid, and sulphuric acid, and dissolves but sparingly in hydrochloric acid. It reddens litmus, even when thoroughly washed. But if we precipitate solution of bichloride of tin with an alkali, or with sulphate of soda, or nitrate of ammonia, we obtain the hydrate of the binoxide *a*, which dissolves readily in hydrochloric acid. Upon ignition, both hydrates lose their water of hydration, and change to binoxide of tin.

Binoxide of tin is a straw-colored powder, which under the influence of heat, transiently assumes a different tint, varying from bright yellow to brown. It is insoluble in water and acids, and does not alter the color of litmus paper. Mixed with chloride of ammonium in excess, and exposed to the action of a red heat, it volatilizes completely as bichloride. If binoxide of tin is fused with cyanide of potassium, all the tin is obtained in form of metallic globules, which may be completely, and without the least loss of metal, freed from the adhering slag, by extracting with dilute spirit of wine and rapidly decanting the fluid off from the tin globules (*H. Rose*, "Journ. f. prakt. Chem,." 61, 189).

COMPOSITION.

$$\begin{array}{rcl} \text{Sn} = 725 = 58 = & 78{\cdot}38 \\ 2\ \text{O} = \underline{200} = \underline{16} = & \underline{21{\cdot}62} \\ 925 = 74 = & 100{\cdot}00 \end{array}$$

b. Hydrated protosulphide of tin forms a brown precipitate, insoluble in water, sulphuretted hydrogen water and dilute acids. Ammonia fails to dissolve it; but it dissolves pretty readily (as bisulphide) in the yellow sulphide of ammonium, and in the yellow sulphide of potassium; it dissolves readily in hot concentrated hydrochloric acid. Heated, with exclusion of air, it loses its water of hydration, and is converted into anhydrous protosulphide of tin; when exposed to the continued action of a gentle heat, with free access of air, it is converted into sulphurous acid, which escapes, and binoxide of tin, which remains.

c. Hydrated bisulphide of tin forms a bright yellow precipitate, which, upon drying, assumes a darker tint. It is insoluble in water, but dissolves slightly in water impregnated with sulphuretted hydrogen; it dissolves with difficulty in ammonia, but readily in potassa and alkaline sulphides, and likewise in hot concentrated hydrochloric acid. When heated, with exclusion of air, it loses its water of hydration, and, at the same time, according to the greater or less degree of heat applied, one-half, or a whole equivalent of sulphur, becoming converted either into sesquisulphide, or into protosulphide of tin; when heated very slowly, with free access of air, it is converted into binoxide of tin, with disengagement of sulphurous acid.

§ 92.

6. ARSENIOUS ACID; and 7. ARSENIC ACID.

ARSENIC is weighed either as ARSENATE OF LEAD, or as TERSULPHIDE OF ARSENIC, or as ARSENATE OF MAGNESIA AND AMMONIA, or as BASIC ARSENATE OF SESQUIOXIDE OF IRON; besides these forms, we have here to examine also ARSENIO-MOLYBDATE OF AMMONIA.

a. Arsenate of lead, in the pure state, is a white powder, which begins to agglutinate into a semi-fused mass when exposed to a gentle red heat, at the same time transitorily acquiring a yellow tint; it fuses when exposed to a higher degree of heat. When strongly ignited, it suffers a slight diminution of weight, losing a small proportion of arsenic acid, which escapes as arsenious acid and oxygen. In analysis we have never occasion to operate upon the pure arsenate of lead, but upon a mixture of it with free oxide of lead.

b. Tersulphide of arsenic forms a precipitate of a rich yellow color; it is insoluble in water,* and but very sparingly soluble in sulphuretted hydrogen water. When boiled with water, or left for several days in contact with that fluid, it undergoes a very trifling decomposition: a trace of arsenious acid dissolves in the water, and a minute proportion of sulphuretted hydrogen is disengaged. This does not interfere, however, with the washing of the precipitate. The precipitate may be dried at 212° F., without suffering decomposition; the whole of the water which it contains is expelled at that temperature. When exposed to a stronger heat, tersulphide of arsenic transitorily assumes a brownish-red color, fuses, and finally rises in vapor, without suffering decomposition. It dissolves readily in alkalies and alkaline sulphides, and also in nitrohydrochloric acid; but it is only slightly soluble in boiling concentrated hydrochloric acid. Red fuming nitric acid converts it into arsenic acid and sulphuric acid.

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* In some experiments which I had occasion to make, in the course of an analysis of the springs of Weilbach ("Chemische Untersuchung der wichtigsten Mineralwasser des Herzogthums Nassau von Dr. Fresenius, V. Schwefelquellen zu Weilbach." Wiesbaden, Kreidel und Niedner. 1856), I found that one part of $As S_3$ dissolves in about 1000000 parts of water.

COMPOSITION.

As =	937·5 =	75 =	60·98
3 S =	600·0 =	48 =	39·02
	1537·5 =	123 =	100·00

c. Arsenate of magnesia and ammonia forms a white, somewhat transparent, fine crystalline precipitate, which has the formula $2\,MgO, NH_4O, AsO_5 + 12\,aq.$

At 212° F., it loses 11 equivalents of water; the formula of the precipitate dried at that temperature is accordingly $2\,MgO, NH_4O, AsO_5 + aq.$ Upon ignition it loses its water and ammonia, and changes to $2\,MgO, AsO_5$. But as the ammoniacal gas exercises a reducing action upon the arsenic acid, the new compound suffers a loss of weight, which is the more considerable the longer the application of a red heat is continued; it amounts to from 4—12 per cent. of the arsenic originally present in the salt (*H. Rose*). Arsenate of magnesia and ammonia dissolves very sparingly in water, one part of the salt dried at 212° F. requiring 4926, one part of the anhydrous salt, 5154 parts of water of 59° F. It is still more sparingly soluble in ammoniated water, one part of the salt dried at 212° F. requiring 9260, one part of the anhydrous salt, 9709 parts of a mixture of one part of liquor of ammonia (0·96 sp. gr.), and 7 parts of water at 59° F. In water containing chloride of ammonium, it is much more readily soluble, one part of the anhydrous salt requiring 1600 parts of a solution of one part of chloride of ammonium in 70 parts of water; and 1044 parts of a solution of one part of chloride of ammonium in 7 parts of water. Presence of ammonia diminishes the solvent capacity of the chloride of ammonium solution: one part of the anhydrous salt requires 2790 parts of a mixture of 60 parts of water, 10 of solution of ammonia (0·96 sp. gr.), and one of chloride of ammonium; and 1810 parts of a mixture of one part of chloride of ammonium, one of caustic ammonia, and 6 of water (*Fränkel*, "J. pr. Chem." 56, 33). Arsenate of magnesia and ammonia, dried at 212° F., contains 60·53 per cent. of arsenic acid, and 21·05 per cent. of magnesia.

d. Arsenate of Sesquioxide of Iron.—The white slimy precipitate, produced by the action of arsenate of soda upon solution of sesquichloride of iron, has the composition $2\,Fe_2O_3, 3\,HO, 3\,AsO_5 + 9\,aq.$ It dissolves in solution of ammonia, imparting a yellow color to the fluid.

Besides this compound, there exist still several others, with larger proportions of sesquioxide of iron; thus we have Fe_2O_3, AsO_5, which falls down + 5 aq. upon the precipitation of arsenic acid with acetate of sesquioxide of iron (*Kotschoubey*); $2\,Fe_2O_3, AsO_5$, which is obtained + 12 aq., when basic-arsenate of protoxide of iron is oxidized with nitric acid, and ammonia added;—$16\,Fe_2O_3, AsO_5$, which forms + 24 aq., upon boiling the less basic compounds with solution of potassa in excess (*Berzelius*). The two latter compounds are not soluble in ammonia; the last is quite like hydrated sesquioxide of iron. In *Berthier's* method of estimating arsenic acid, we obtain mixtures of these different salts. They are, on account of their insolubility in ammonia, the better adapted for the purpose, the more basic they are; and at the same time they are more easily washed. Upon ignition the water alone is expelled, provided the heat be very gradually increased. But if the salt is suddenly exposed to a very strong heat, before the adhering ammonia has escaped, part of the arsenic acid is thereby reduced to arsenious acid (*H. Rose*).

e. Arsenio-molybdate of Ammonia.—If a fluid containing arsenic acid is mixed with a large proportion of molybdate of ammonia, and sufficient nitric or hydrochloric acid to redissolve the precipitate of molybdic acid which forms at first, and the fluid heated to boiling, a yellow precipitate of arsenio-molybdate of ammonia separates—provided the molybdic acid be present in excess. This precipitate comports itself with solvents like the analogous compound of phosphoric acid; it is, like the latter, insoluble in water, salts, and free acids, particularly nitric acid, provided an excess of solution of molybdate of ammonia, mixed with acid in moderate excess, be present. *Seligsohn* ("Journ. f. prakt. Chem." 67, 481) found it to be composed of 87·666 per cent. of molybdic acid, 6·308 arsenic acid, 4·258 ammonia, and 1·768 water.

B. — FORMS AND COMBINATIONS IN WHICH THE VARIOUS ACIDS ARE SEPARATED FROM OTHER BODIES, OR IN WHICH THEIR RESPECTIVE WEIGHT IS DETERMINED.

ACIDS OF THE FIRST GROUP.

§ 93.

1. ARSENIOUS ACID and ARSENIC ACID.—See the preceding paragraph (§ 92).

2. CHROMIC ACID.

Chromic acid is weighed either in the form of SESQUIOXIDE OF CHROMIUM, or in that of CHROMATE OF LEAD.

a. Sesquioxide of Chromium.—See § 76.

b. Chromate of lead forms a bright yellow precipitate, insoluble in water and in acetic acid, and barely soluble in dilute nitric acid, but readily so in solution of potassa. When chromate of lead is boiled with concentrated hydrochloric acid, it is readily decomposed, and, its elements transposing with those of the decomposing acid, chloride of lead and sesquichloride of chromium are formed. Addition of alcohol tends to promote this double decomposition. Chromate of lead is unalterable in the air; it dries thoroughly at 212° F. Under the influence of heat it transitorily acquires a reddish-brown tint; it fuses at a red heat; when heated beyond its point of fusion, it loses oxygen, and is transformed into a mixture of sesquioxide of chromium and basic chromate of lead. Heated in contact with organic substances, it readily yields oxygen to the latter.

COMPOSITION.

$$\begin{array}{lrrr} \mathrm{Pb\,O} & = 1394{\cdot}64 = & 111{\cdot}57 = & 68{\cdot}72 \\ \mathrm{Cr\,O_3} & = \quad 634{\cdot}70 = & 50{\cdot}78 = & 31{\cdot}28 \\ \hline & 2029{\cdot}34 = & 162{\cdot}35 = & 100{\cdot}00 \end{array}$$

3. SULPHURIC ACID.

Sulphuric acid is determined best in the form of SULPHATE OF BARYTA, for the properties of which see § 71.

4. PHOSPHORIC ACID.

Phosphoric acid may be weighed as PHOSPHATE OF LEAD, PYROPHOS-

PHATE OF MAGNESIA, BASIC PHOSPHATE OF MAGNESIA ($3\,MgO, PO_5$), BASIC PHOSPHATE OF SESQUIOXIDE OF IRON, PHOSPHATE OF SESQUIOXIDE OF URANIUM, PHOSPHATE OF BINOXIDE OF TIN, PHOSPHATE and PYROPHOSPHATE OF SILVER. Besides these compounds, we have to examine PHOSPHATE OF SUBOXIDE OF MERCURY, and PHOSPHO-MOLYBDATE OF AMMONIA.

a. The *phosphate of lead* obtained in the course of analysis is rarely quite pure, but is generally mixed with free oxide of lead. In this mixture we have accordingly the basic phosphate of lead ($3\,PbO, PO_5$); in the pure state, this presents the appearance of a white powder; it is insoluble in water and in acetic acid, and equally so in ammonia; it dissolves readily in nitric acid. When exposed to the action of heat, it fuses, without undergoing decomposition.

b. Pyrophosphate of Magnesia.—See § 74.

c. Basic Phosphate of Magnesia ($3\,MgO, PO_5$).—This compound is produced by mixing a solution of an alkaline phosphate, containing chloride of ammonium, with magnesia, evaporating the mixture, heating the residue until the chloride of ammonium is completely expelled, and finally treating with water; the compound so produced contains an excess of magnesia. It is sufficient for our purpose to state that it is nearly absolutely insoluble in water and in solutions of salts of the alkalies (*Fr. Schulze*, "Journ. f. prakt. Chem.," 63, 440).

d. Basic Phosphate of Sesquioxide of Iron.

Räwsky states that upon the precipitation of phosphoric acid with acetate of sesquioxide of iron in excess, or with a mixture of iron alum and acetate of soda, a phosphate of sesquioxide of iron is produced, of constant composition, viz., Fe_2O_3, PO_5. The correctness of this statement has been questioned, in *Liebig* and *Kopp's* "Annual Report" ("Jahresbericht"), 1847 and 1848, p. 946; and altogether disputed by *Way* and *Ogston* (*Liebig* and *Kopp's* "Annual Report," 1849, p. 571). *Wittstein* obtained $Fe_2O_3. PO_5$, by exactly precipitating phosphoric acid with acetate of sesquioxide of iron; but upon adding the precipitant in excess, he obtained $4\,Fe_2O_3, 3\,PO_5$. *Rammelsberg* obtained $Fe_2O_3, PO_5 + 4$ aq., and *Wittstein* subsequently, the same compound + 8 aq., upon mixing sulphate of sesquioxide of iron with phosphate of soda in excess; with an insufficient quantity of the phosphate of soda, the latter chemist obtained a more yellowish precipitate, which had the formula

$$3\,(Fe_2O_3, PO_5 + 8\,\text{aq.}) + (Fe_2O_3, 3\,HO).$$

If an acid fluid containing a *considerable* excess of phosphoric acid is mixed with a small portion of sesquioxide of iron, and an alkaline acetate added, there is also obtained simply an analogous precipitate, viz., Fe_2O_3, PO_5 + water, which, accordingly, leaves upon ignition $Fe_2O_3, 3\,PO_5$, (*Wittstein*).

Fresh experiments made by me upon this subject have positively convinced me of the perfect correctness of *Wittstein's* statement.*

COMPOSITION.

$$\begin{array}{lrrr} PO_5 = & 887{\cdot}50 = & 71 = & 47{\cdot}02 \\ Fe_2O_3 = & 1000{\cdot}00 = & 80 = & 52{\cdot}98 \\ \hline & 1857{\cdot}50 = & 151 = & 100{\cdot}00 \end{array}$$

---

* In an experiment made at a former period by *Will* and myself ("Annal. der Chem. u. Pharm.," 50, 379), we obtained a precipitate of the formula $2\,Fe_2O_3, 3\,PO_5 + 3\,HO + 10$ aq.; but I have never since succeeded in producing a precipitate of the same composition.

If we dissolve phosphate of sesquioxide of iron in hydrochloric acid, supersaturate the solution with ammonia, and apply heat, we obtain more basic salts, viz., $3\,Fe_2O_3, 2\,PO_5$ (*Rammelsberg*); $2\,Fe_2O_3, PO_5$ (*Wittstein*—after long washing). In *Wittstein's* experiment, the washing fluid contained phosphoric acid. The white phosphate of sesquioxide of iron does not dissolve in acetic acid, but readily in a solution of acetate of sesquioxide of iron.

Upon boiling the latter solution (of phosphate of sesquioxide of iron in acetate of sesquioxide of iron), the whole of the phosphoric acid precipitates, together with the basic acetate of sesquioxide of iron, as *hyperbasic phosphate of sesquioxide of iron* ($15\,Fe_2O_3, PO_5$—*Rammelsberg*). The hyperbasic phosphate of sesquioxide of iron is invariably obtained, mixed with free hydrated sesquioxide of iron, upon precipitating with ammonia or carbonate of baryta a solution containing phosphoric acid and an excess of sesquioxide of iron. The precipitate is insoluble, or, more correctly speaking, most difficultly and sparingly soluble, in water and in ammonia. Sulphide of ammonium, added to the fluid filtered off from the precipitate, imparts to the filtrate, after some time standing, a greenish tint. Upon washing the precipitate with cold water, the latter speedily runs off yellow; this coloration is still more marked when ammoniated water is used (*H. Rose*).

e. Phosphate of Sesquioxide of Uranium.—If the hot aqueous solution of a phosphate soluble in water or acetic acid is mixed, in presence of free acetic acid, with acetate of sesquioxide of uranium, a precipitate of phosphate of sesquioxide of uranium is immediately formed. If the fluid contains an ammoniacal salt in somewhat large proportions, the precipitate contains also ammonia. The same precipitate forms also if alumina or sesquioxide of iron is present; but in that case it is always more or less mixed with phosphate of sesquioxide of iron or phosphate of alumina.

Phosphate of sesquioxide of uranium is a somewhat gelatinous, whitish-yellow precipitate, with a tinge of green. The best way of washing it, at least so far as the principal part of the operation is concerned, is to boil with water and decant the fluid. If, after having allowed the fluid in which the precipitate is suspended to cool a little, a few drops of chloroform are added, and the mixture is shaken or boiled up, the precipitate subsides much more readily than without this addition.

The precipitate is insoluble in water and in acetic acid; but it dissolves in mineral acids; acetate of ammonia, added in sufficient excess, completely re-precipitates it from this solution, upon application of heat. Upon igniting the precipitate, no matter whether containing ammonia or not, phosphate of sesquioxide of uranium of the formula $2\,(Ur_2O_3), PO_5$ is produced. This has the color of the yolk of an egg. If the precipitate is ignited in presence of charcoal or of some reducing gas, partial reduction to phosphate of protoxide of uranium ensues, owing to which the ignited mass acquires a greenish tint; however, upon warming the greenish residue with some nitric acid, the green salt of the protoxide is readily re-converted into the yellow salt of the sesquioxide. Phosphate of sesquioxide of uranium is not hygroscopic, and may therefore be ignited and weighed in an open platinum dish (*A. Arendt* and *W. Knop*, "Chemisches Centralblatt," 1856, 769, 803; and 1857, 177).

COMPOSITION.

$$\begin{array}{lrrrr} 2\,Ur_2O_3 & =3571{\cdot}48 & =285{\cdot}6 & = & 80{\cdot}09 \\ P\,O_5 & = \;887{\cdot}50 & = \;71{\cdot}0 & = & 19{\cdot}91 \\ \hline & 4458{\cdot}98 & =356{\cdot}6 & = & 100{\cdot}00 \end{array}$$

The one-fifth part of the precipitate may accordingly be calculated as phosphoric acid.

f. Phosphate of binoxide of tin is never obtained in the pure state in the analytical process, but contains always an admixture of hydrated metastannic acid in excess, which, upon ignition, changes to metastannic acid. It has, generally speaking, the same properties as hydrated metastannic acid, and is more particularly, like the latter, insoluble in nitric acid. Upon heating with concentrated solution of potassa, phosphate and metastannate of potassa are formed.

g. Tribasic phosphate of silver is a powder of a bright yellow color; it is insoluble in water, but readily soluble in nitric acid, and also in ammonia. In ammoniacal salts, it is difficultly soluble. It is unalterable in the air. Upon ignition, it acquires transiently a reddish brown color; at an intense red heat, it fuses without decomposition.

COMPOSITION.

$$\begin{array}{lrrrr} 3\,Ag\,O & =4348{\cdot}98 & =347{\cdot}91 & = & 83{\cdot}05 \\ P\,O_5 & = \;887{\cdot}50 & = \;71{\cdot}00 & = & 16{\cdot}95 \\ \hline & 5236{\cdot}48 & =418{\cdot}91 & = & 100{\cdot}00 \end{array}$$

h. Pyrophosphate of silver is a white powder, unalterable and insoluble in water, even upon ebullition; but readily soluble in ammonia, and also in nitric acid. It is unalterable in the air. Exposed to a heat somewhat below redness, it fuses, without decomposition, to a dark, brown liquid, which, upon cooling, solidifies to a white, radiated mass.

COMPOSITION.

$$\begin{array}{lrrrr} 2\,Ag\,O & =2899{\cdot}32 & =231{\cdot}94 & = & 76{\cdot}56 \\ b\,P\,O_5 & = \;887{\cdot}50 & = \;71{\cdot}00 & = & 23{\cdot}44 \\ \hline & 3786{\cdot}82 & =302{\cdot}94 & = & 100{\cdot}00 \end{array}$$

i. Phosphate of Suboxide of Mercury.—This compound is employed for the purpose of effecting the separation of phosphoric acid from many bases, after *H. Rose's* method.

Phosphate of suboxide of mercury presents the appearance of a white crystalline mass, or of a white powder. It is insoluble in water, but dissolves in nitric acid. The action of a red heat converts it into fused phosphate of oxide of mercury, with evolution of mercurial fumes. Upon fusion with alkaline carbonates, alkaline phosphates are produced, and mercurial fumes escape.

k. Phospho-molybdate of Ammonia.—This compound also serves to effect the separation of phosphoric acid from other bodies; it is of the utmost importance in this respect.

Phospho-molybdate of ammonia forms a bright yellow, readily subsiding precipitate, which, according to *Seligsohn* has the following (average) composition.

Molybdic acid	90·744
Phosphoric acid.	3·142
Oxide of ammonium	3·570
Water	2·544
	100·000

In the pure state, it dissolves but sparingly in cold water; but it is soluble in hot water. It is readily soluble, even in the cold, in caustic alkalies, alkaline carbonates and phosphates, chloride of ammonium, and oxalate of ammonia. It dissolves only sparingly in sulphate of ammonia, nitrate of potassa, and chloride of potassium; and very sparingly in nitrate of ammonia.

It is soluble in sulphate of potassa and sulphate of soda, chloride of sodium and chloride of magnesium, sulphuric, hydrochloric, and nitric acids (both concentrated and dilute). Application of heat does not check the solvent action of these substances. Presence of molybdate of ammonia totally changes the deportment of the phospho-molybdate of ammonia with solvents: in presence of that substance, the latter compound is almost insoluble in acids, even upon ebullition. The solution of the phospho-molybdate of ammonia in acids is probably attended, in all cases, with decomposition and with separation of the molybdic acid, which decomposition and separation the presence of molybdate of ammonia prevents (*J. Craw*, "Chem. Gaz.," 1852, 216).

5. Boracic Acid.

Borofluoride of Potassium is the best form to convert boracic acid into for the purpose of the direct estimation of the acid. This compound is produced by mixing the solution of an alkaline borate (the potassa salt answers best) with hydrofluoric acid in excess, in a silver or platinum dish, and evaporating to dryness. The gelatinous precipitate which forms in the cold, dissolves upon application of heat, and separates from the solution subsequently, upon evaporation, in small, hard, transparent crystals. The compound has the formula $K\,Fl, B\,Fl_3$. It is soluble in water and also in dilute spirit of wine; but strong alcohol fails to dissolve it; it is insoluble also in concentrated solution of acetate of soda. It may be dried at 212° F., without suffering decomposition (*Aug. Stromeyer*, "Annal. d. Chem. u. Pharm.," 100, 82).

COMPOSITION.

$$
\begin{array}{lrrr}
K & = 488{\cdot}86 = & 39{\cdot}11 = & 31{\cdot}00 \\
B & = 138{\cdot}05 = & 11{\cdot}04 = & 8{\cdot}75 \\
Fl_4 & = 950{\cdot}00 = & 76{\cdot}00 = & 60{\cdot}25 \\
\hline
 & 1576{\cdot}91 = & 126{\cdot}15 = & 100{\cdot}00
\end{array}
$$

6. Oxalic Acid.

Oxalic acid is usually precipitated in the form of oxalate of lime; and its weight is generally inferred from the CARBONATE OF LIME produced from the oxalate by ignition. For the properties, &c., of carbonate of lime and of oxalate of lime, see § 73.

7. Hydrofluoric Acid.

The *direct* estimation of hydrofluoric acid is uniformly effected by weighing the acid in the form of FLUORIDE OF CALCIUM.

Fluoride of calcium forms a gelatinous precipitate, which it is found difficult to wash. If digested with ammonia, previous to filtration, it is rendered denser and less gelatinous. It is not altogether insoluble in water; aqueous solutions of the alkalies fail to decompose it. It is very slightly soluble in dilute, but more readily in concentrated hydrochloric acid. When acted upon by sulphuric acid, it is decomposed, and sulphate of lime and hydrofluoric acid are formed. Fluoride of calcium is unalterable in the air, and at a red heat. Heated to very intense redness, it fuses. Upon ignition in moist air, it is slowly and partially decomposed into lime and hydrofluoric acid. Mixed with chloride of ammonium, and exposed to a red heat, fluoride of calcium suffers a constant loss of weight; but the decomposition is incomplete.

COMPOSITION.

$$\begin{array}{lllll} \mathrm{Ca} & = 250{\cdot}0 & = 20 & = & 51{\cdot}28 \\ \mathrm{Fl} & = 237{\cdot}5 & = 19 & = & 48{\cdot}72 \\ \hline & 487{\cdot}5 & = 39 & = & 100{\cdot}00 \end{array}$$

8. Carbonic Acid.

The *direct* estimation of carbonic acid—which, however, is only rarely resorted to—is usually effected by weighing the acid in the form of CARBONATE OF LIME. For the properties of the latter substance, see § 73.

9. Silicic Acid.

Silicic acid is always weighed in its insoluble modification.

The insoluble modification of silicic acid, artificially prepared, is a white powder, insoluble in water and in acids, but soluble in solution of potassa and in solutions of the carbonates of the fixed alkalies. It is perfectly unalterable in the air, and at a red heat, and requires the very highest degrees of heat for its fusion. It does not affect vegetable colors. It dissolves in hydrofluoric acid; if the silicic acid is pure, the solution leaves no residue upon evaporation on platinum.

Upon evaporating a solution of the soluble modification of silicic acid in water, or in any volatile acid (hydrofluoric acid excepted), we obtain the silicic acid at first as a gelatinous hydrate; this, upon drying in the air, loses part of its water, and is converted into $3\ \mathrm{Si\,O_2,\ H\,O}$; dried at 212° F., it changes to $4\ \mathrm{Si\,O_2,\ H\,O}$ (*J. Fuchs*). This latter compound presents the appearance of a loose, white powder, which, upon exposure to a red heat, loses the whole of its water; the escaping aqueous vapor is apt to carry away particles of the exceedingly fine powder.

Artificially prepared silicic acid, when exposed to a red heat, mixed with chloride of ammonium, loses weight at first; but after a time, when the action of the heat has given greater density to the acid, this loss is completely checked.

COMPOSITION.

$$\begin{array}{lllll} \mathrm{Si} & = 185{\cdot}18 & = 14{\cdot}81 & = & 48{\cdot}08 \\ 2\,\mathrm{O} & = 200{\cdot}00 & = 16{\cdot}00 & = & 51{\cdot}92 \\ \hline & 385{\cdot}18 & = 30{\cdot}81 & = & 100{\cdot}00 \end{array}$$

The gelatinous (but not the pulverulent) hydrate of silicic acid is slightly soluble in water and in hydrochloric acid. The degree of solubility depends upon the circumstance whether the gelatinous hydrate has just been thrown down or has already acquired a higher degree of density. 1 part of the silicic acid obtained by transmitting fluoride of silicon gas through water, and thoroughly washing the precipitate produced, dissolves in 7700 parts of water; in 11000 parts of cold, and 5500 parts of boiling hydrochloric acid of 1·115 sp. gr. (*J. Fuchs*).

ACIDS OF THE SECOND GROUP.

§ 94.

1. Hydrochloric Acid.

Hydrochloric acid is almost invariably determined in the form of CHLORIDE OF SILVER—for the properties of which, see § 82.

2. Hydrobromic Acid.

Hydrobromic acid is always determined in the form of BROMIDE OF SILVER.

Bromide of silver, prepared in the humid way, forms a yellowish-white precipitate. It is wholly insoluble in water and in nitric acid, but tolerably soluble in ammonia; it dissolves in hot solution of chloride of ammonium, but very sparingly in solution of nitrate of ammonia. When acted upon by chlorine, no matter whether in the dry or in the humid way, it is decomposed, chloride of silver being formed, with separation of bromine. Exposed to the light, it gradually turns gray, and finally black. Under the influence of heat, it fuses to a reddish liquid, which, upon cooling, solidifies to a yellow horn-like mass. Brought into contact with zinc and water, bromide of silver is decomposed: a spongy mass of metallic silver forms, and the solution contains bromide of zinc.

COMPOSITION.

Ag = 1349·66 = 107·97 = 57·46
Br = 999·62 = 79·97 = 42·54

2349·28 = 187·94 = 100·00

3. Hydriodic Acid.

Hydriodic acid is usually determined in the form of IODIDE OF SILVER, and occasionally also in that of PROTIODIDE OF PALLADIUM.

a. Iodide of silver, produced in the humid way, forms a bright yellow precipitate, insoluble in water and in dilute nitric acid, and very slightly soluble in ammonia. It is decomposed by chlorine, both in the dry and in the humid way. Hot concentrated nitric and sulphuric acids convert it, but with some difficulty, into the corresponding nitrate and sulphate of silver, with expulsion of the iodine. Iodide of silver acquires a black color when exposed to the light. When heated, it fuses without decomposition to a reddish fluid, which, upon cooling, solidifies to a yellow mass, that may be cut with a knife. When brought into contact with zinc and water, it is decomposed: iodide of zinc is formed, and metallic silver separates.

COMPOSITION.

Ag = 1349·66 = 107·97 = 45·98
I = 1586·00 = 126·88 = 54·02

2935·66 = 234·85 = 100·00

b. Protiodide of palladium, produced by precipitating a solution of the iodide of one of the fixed alkalies with protochloride of palladium, is a deep brownish-black, flocculent mass, insoluble in water, and in dilute hydrochloric acid, but slightly soluble in saline solutions (solution of chloride of sodium, chloride of magnesium, chloride of calcium, &c.). It is unalterable in the air. Dried simply in the air, it retains one equivalent of water = 5·05 per cent. Dried long in vacuo, or at a high temperature (158° to 176° F.), it yields the whole of this water, without the least loss of iodine. Dried at 212° F., it loses a trace of iodine; at from 572° to 752° F., the whole of the iodine is expelled. The precipitated iodide of palladium may be washed with hot water, without loss of iodine.

COMPOSITION.

$$\begin{array}{lrcrcr} \mathrm{Pd} = & 665{\cdot}48 & = & 53{\cdot}24 & = & 29{\cdot}57 \\ \mathrm{I} = & 1586{\cdot}00 & = & 126{\cdot}88 & = & 70{\cdot}43 \\ \hline & 2251{\cdot}48 & = & 180{\cdot}12 & = & 100{\cdot}00 \end{array}$$

4. HYDROCYANIC ACID.

The *direct* estimation of hydrocyanic acid is always effected by weighing that acid in the form of CYANIDE OF SILVER—for the properties of which compound, see § 82.

5. HYDROSULPHURIC ACID.

Sulphuretted Hydrogen.

The forms into which sulphuretted hydrogen, or the sulphur in metallic sulphides, is converted for the purpose of quantitative estimation, are TERSULPHIDE OF ARSENIC, SULPHIDE OF SILVER, SULPHIDE OF COPPER, and SULPHATE OF BARYTA.

For the properties of the sulphides named, see §§ 82, 85, 92; for those of sulphate of baryta, see § 71.

ACIDS OF THE THIRD GROUP.

§ 95.

1. NITRIC ACID; and 2. CHLORIC ACID.

These two acids are never estimated in a *direct* way, that is to say, in compounds containing them, but always in an *indirect* way; often volumetrically.

* * *

SECTION IV.

IN the preceding section we have examined the composition and properties of the various forms and combinations in which substances are separated from others, or in which their weight is estimated. We have now to consider the special means and methods of converting substances into such forms and combinations.

For the sake of greater clearness and simplicity, we divide this part of the work into two sections, confining ourselves, in the first, to the exposition of the various methods applied to effect the *quantitative estimation of substances*, and deferring to the next section the consideration of the means best adapted for the *separation of substances from one another*.

QUANTITATIVE DETERMINATION, OR ESTIMATION OF THE WEIGHT OF SUBSTANCES.*

§ 96.

We have to deal here exclusively with compounds consisting of *one base and one acid*, or of *one metal and one metalloid*.

In the quantitative estimation of substances, we have to study two points, viz., first, the most appropriate manner of dissolving the substance we wish to analyse, either in its isolated state, or in its various combinations,—ITS SOLUTION; and secondly, the methods best adapted to obtain the substance in a ponderable form, or generally to estimate its quantity, —THE DETERMINATION OF ITS WEIGHT.

With regard to the latter point, we have to turn our attention, 1, to the *practical performance* of the several processes and operations constituting the special method or methods applied in every individual case; and 2, to the greater or less degree of *accuracy* attainable by the several methods.

It happens very rarely in quantitative analyses that the amount of a substance, as determined by the analytical process, corresponds exactly with the amount theoretically calculated.

The cause of this almost invariably occurring discrepancy between the quantity calculated and that actually found, is to be ascribed either exclusively to *certain unavoidable defects inherent in the execution of the necessary processes and operations*, or it lies partly in the *method itself*.

The *execution* of the analytical processes and operations can never be *absolutely* accurate, even though the greatest care and attention be bestowed on the most trifling minutiæ. To account for this, we need only bear in mind that our weights and measures are never *absolutely* correct, nor our balances *absolutely* accurate, nor our reagents *absolutely* pure, and moreover, that we do not weigh *in vacuo*; and that, even if we deduce the weight we might expect to obtain by weighing *in vacuo* from the weight we *actually* obtain by weighing in the air, we can only *approximate*, but never *attain* absolutely accurate figures;—that the hygroscopic state of the air is liable to vary between the moment of weighing the crucible whilst empty and that of weighing the crucible after having introduced the substance to be analysed;—that we know the weight of the ashes of our filters only *approximately*;—that, upon the evaporation of many fluids, traces of salts will volatilize which, in their solid state, are considered perfectly fixed;—that absolute perfection cannot be attained in the operation of washing and rinsing;—that we can never succeed in sheltering the contents of dishes and crucibles, &c., *absolutely* from dust, &c. &c.

With regard to the *methods*, many of them are not entirely free from certain unavoidable *sources of error*;—precipitates are not *absolutely* insoluble; compounds which require ignition are not *absolutely* fixed; others, which require drying, have a slight tendency to volatilize; the final reaction in volumetrical analyses is usually produced only by a small excess of the standard fluid, which is occasionally liable to vary with the degree of dilution, the temperature, &c. &c.

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* By the volumetric as well as by the gravimetric method.

Strictly speaking, no method can be pronounced quite free from defect; it should be borne in mind, for example, that even *sulphate of baryta* is not *absolutely* insoluble in water.

We have, therefore, in our analytical processes, invariably to contend against certain sources of inaccuracy which it is impossible to overcome entirely, even though our operations be conducted with the most scrupulous care and with the utmost attention to established rules. It will be readily understood that several defects and sources of error may, in some cases, *combine* to vitiate the results; whereas, in other cases, they may *compensate* one another, and thus enable us to attain a higher degree of accuracy. The *comparative* accuracy of the results attainable by an analytical method oscillates between two points or limits, fixed respectively on either side of the point of *absolute* accuracy. In the case of methods relatively free from defects and sources of error, these limits will closely approximate the medium point of absolute accuracy; thus, for instance, in the quantitative estimations of chlorine, a careful operator will always be able to obtain between 99·9 and 100·1, for the 100 parts of chlorine theoretically calculated.

Less perfect methods will, of course, exhibit far greater discrepancies; thus, in the estimation of strontia, the most attentive and skilful operator may not be able to obtain more than 99·0 (and even less) for the 100 parts of strontia theoretically calculated. I may here incidentally state, that the numbers occasionally given in this manner, in the course of the present work, to denote the respective and relative accuracy of certain methods, refer invariably to the substance estimated (chlorine, nitrogen, baryta), and not to the forms and combinations in which that substance may happen to be weighed (chloride of silver, bichloride of platinum and chloride of ammonium, sulphate of baryta).

The occasional attainment of results *exactly* corresponding with the numbers calculated does not always justify the assumption, on the part of the analyst, that his operations, to have led to such a result, must have been conducted with the utmost precision and accuracy. It may sometimes happen, in the course of the analytical process, that one error serves to compensate another; thus, for instance, the analyst may, at the commencement of his operations, spill a minute portion of the substance to be analysed; whilst, at a later stage of the process, he may recover the loss by an imperfect washing of the precipitates. As a general rule, results showing a trifling deficiency of substance may be looked upon as better proof of accurate performance of the analytical process, than results exhibiting an excess of substance.

As not the least effective means of guarding against error and inaccuracies in *gravimetric analyses*, I would most strongly recommend the student *always carefully to mark the appearance and properties of the weighed substance, and to compare them with those which that substance ought to exhibit,* and which have been amply described in the preceding section.

In my own laboratory, I insist upon all substances that are weighed in the course of an analysis being kept between watch-glasses, until the whole process is concluded. This affords always a chance of testing them once more for some admixture or impurity, of which the presence may become suspected in the after course of the process.

I. QUANTITATIVE ESTIMATION OF BASES IN COMPOUNDS CONTAINING ONLY ONE BASE AND ONE ACID, OR ONE METAL AND ONE METALLOID.

FIRST GROUP.

POTASSA—SODA—OXIDE OF AMMONIUM—(LITHIA).

§ 97.

1. Potassa.

a. Solution.

Potassa and its salts with those inorganic acids which we have to consider here are dissolved in water, in which menstruum they dissolve readily, or at all events, pretty readily.

Potassa salts with organic acids are first converted into carbonate of potassa by long-continued ignition in covered crucibles.

b. Quantitative Estimation.

Potassa is weighed either as *sulphate* or *nitrate of potassa*, or as *chloride of potassium* or *bichloride of platinum and chloride of potassium* (see § 68). For the alkalimetrical estimation of free potassa or carbonate of potassa, see §§ 219 and 220.

We may convert into

1. Sulphate of Potassa.

Salts of potassa with strong volatile acids; *e. g.* chloride of potassium, bromide of potassium, nitrate of potassa, &c.

2. Nitrate of Potassa.

Caustic potassa, and compounds of potassa with weak volatile acids that are not decomposed by nitric acid; *e. g.* carbonate of potassa (salts of potassa with organic acids).

3. Chloride of Potassium.

In general, caustic potassa and salts of potassa with weak volatile acids, especially also with such as are decomposed by nitric acid; *e. g.* sulphide of potassium.

Also, and more particularly, sulphate, chromate, chlorate, and silicate of potassa.

4. Bichloride of Platinum and Chloride of Potassium.

Salts of potassa with non-volatile acids soluble in alcohol; *e. g.* phosphate of potassa, borate of potassa.

The potassa in the borate of that alkali may be determined also as sulphate (§ 136); and the potassa in the phosphate, as chloride of potassium (§ 134).

The form of bichloride of platinum and chloride of potassium may also be resorted to in general, for the quantitative estimation of the potassa in all salts of that alkali with acids soluble in alcohol. This form is, moreover, of especial importance here, as that in which the separation of potassa from soda, &c., is effected.

1. *Determination as Sulphate of Potassa.*

Evaporate the aqueous solution of the sulphate of potassa to dryness, ignite the residue in a platinum crucible or dish, and weigh (§ 42). The residue must be thoroughly dried, before you proceed to ignite it;

the heat applied for the latter purpose must be moderate at first, and very gradually increased to the requisite degree; the crucible or dish must be kept well covered—neglect of these precautionary rules involves always a loss of substance from decrepitation. If free sulphuric acid is present, we obtain, upon evaporation, bisulphate of potassa; in such cases the excess of sulphuric acid is to be removed by addition of carbonate of ammonia. See § 68.

For properties of the residue, see § 68. Observe more particularly that the residue must dissolve to a clear fluid, and that the solution must be neutral. Should traces of platinum remain behind, these must be carefully weighed, and their weight subtracted from that of the ignited residue.

With proper care and attention, this method gives accurate results.

To convert the salts above mentioned, chloride of potassium, &c., into sulphate of potassa, add to their aqueous solution a quantity of pure sulphuric acid more than sufficient to saturate the whole of the potassa, evaporate the solution to dryness, ignite the residue, and convert the bisulphate of potassa into the neutral salt, by treating with carbonate of ammonia (§ 68).

As the expulsion of a large quantity of sulphuric acid is a very disagreeable process, avoid adding too great an excess. Should too little of the acid have been used, which you will learn from the cessation of the disengagement of sulphuric acid fumes towards the end of the process of ignition, moisten the residue with dilute sulphuric acid, evaporate, and again ignite. If you have to deal with a small quantity only of chloride of potassium, &c., proceed at once to treat the dry salt, cautiously, with dilute sulphuric acid in the platinum crucible; provided always the latter be capacious enough. In the case of bromide of potassium and iodide of potassium, the use of platinum vessels must be avoided.

2. *Determination as Nitrate of Potassa.*

General method the same as described in 1. Nitrate of potassa must be heated very gently to the fusing point, otherwise some loss is likely to arise from evolution of oxygen.

For properties of the residue, see § 68. The method is easy; and the results accurate.

In the conversion of carbonate of potassa into the nitrate, § 38 must be consulted.

3. *Determination as Chloride of Potassium.*

General method the same as described in 1. The residue of chloride of potassium must, previously to ignition, be treated in the same way as sulphate of potassa, and for the same reason. The salt must be heated in a well-covered crucible, and only to dull redness, as the application of a higher degree of heat is likely to cause some loss by volatilization. No particular regard need be had to the presence of free acid. For properties of the residue, see § 68. This method, if properly and carefully executed, gives very accurate results. The potassa in the carbonate of that alkali is, as stated above, generally determined in the form of nitrate of potassa. However, as the residue of carbonate of potassa which remains in the crucible upon the ignition of potassa salts containing organic acids, is apt to effervesce in the process of its conversion into nitrate, which effervescence it is often desirable to avoid, the carbonate of potassa may be determined in the form of chloride of potassium, instead of that of nitrate of potassa. The conversion of the carbonate into chloride of potassium is effected by treating the former with solution of chloride of ammonium, slightly in excess, evaporating the mixture, and igniting the residue, when carbonate of ammonia and the excess of chloride of ammonium will escape, leaving chloride of potassium behind.

The methods of converting into chloride of potassium the potassa compounds specified in 3, will be found in Part II. of this section, under the respective heads of the acids which they contain.

4. *Determination as Bichloride of Platinum and Chloride of Potassium.*

a. Salts of potassa with volatile acids (nitric acid, acetic acid, &c.).

Mix the solution with hydrochloric acid, evaporate to dryness, dissolve the residue in water, add a concentrated solution of bichloride of platinum, as neutral as possible, in excess, and evaporate in a porcelain dish, on the water-bath, nearly to dryness, taking care not to heat the water-bath quite to boiling. Pour spirit of wine of about 80 per cent. over the residue; let it stand for some time, and then put the bichloride of platinum and chloride of potassium, which remains undissolved, upon a weighed filter (which may be readily done by means of a washing bottle filled with spirit of wine). Wash with spirit of wine, dry at 212° F., and weigh (§ 50).

β. Potassa salts with non-volatile acids, phosphoric acid, boracic acid, &c.

Make a concentrated solution of the salt in water, add some hydrochloric acid, and bichloride of platinum in excess, mix with a proper quantity of the strongest alcohol, let the mixture stand 24 hours; after which filter, and proceed as directed in *a.* For properties of the precipitate, see § 68. This method, if properly and carefully executed, gives satisfactory results.* Still there is generally a trifling loss of substance, bichloride of platinum and chloride of potassium not being absolutely insoluble even in strong alcohol. In accurate analyses, therefore, the alcoholic washings must be evaporated, with addition of a little pure chloride of sodium, at a temperature not exceeding 167° F., nearly to dryness, and the residue treated once more with spirit of wine. A trifling additional amount of bichloride of platinum and chloride of potassium is thus obtained, which is either added to the principal precipitates or collected on a separate small filter, and determined as platinum, by the method given below. The object of the addition of a little chloride of sodium to the bichloride of platinum, is to obviate the decomposition to which pure bichloride of platinum is more liable, upon evaporation in alcoholic solution, than the bichloride containing sodio-bichloride of platinum.

As collecting a precipitate upon a weighed filter is a rather tedious process, and, besides, not over accurate, where we have to deal with minute quantities of substance, it is better to collect trifling portions (up to about 0·03 grm.) of bichloride of platinum and chloride of potassium upon a very small *unweighed* filter, dry, and transfer the filter, with the precipitate wrapped up in it, to a small platinum crucible. Cover the crucible, and let the filter slowly char; remove the cover, burn the charcoal of the filter, and let the crucible get cold. Put now a very minute portion of pure oxalic acid into the crucible, cover, and ignite, gently at first. finally to a strong red heat. The addition of the oxalic acid greatly promotes the complete decomposition of the bichloride of platinum and chloride of potassium, which cannot well be effected by simple ignition. Treat the contents of the crucible now with water, and wash the residuary platinum, until the last rinsings remain clear upon addition of solution of nitrate of silver.* Dry the residuary platinum, ignite, and weigh. One equivalent of platinum represents one equivalent of potassium.

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* The atmosphere of a laboratory is very apt to be more or less strongly ammoniacal. This is a circumstance of some importance, and which must not be lost sight of in this process, since, if the influence of an atmosphere of this kind be not properly guarded against, bichloride of platinum and chloride of ammonium may form, which would tend to make the weight of the bichloride of platinum and chloride of potassium appear greater than it really is.

§ 98.

2. SODA.

a. Solution.

See § 97, *a*—solution of potassa—all the directions given in that place applying equally to the solution of soda and its salts.

b. Determination.

Soda is determined either as *sulphate of soda* or *nitrate of soda*, or as *chloride of sodium* or as *carbonate of soda* (§ 69). For the alkalimetrical estimation of caustic soda, and carbonate of soda, see §§ 219 and 220.

We may convert into

1. SULPHATE OF SODA; 2. NITRATE OF SODA; 3. CHLORIDE OF SODIUM.

In general the salts of soda corresponding to the salts of potassa specified under the same heads in § 97.

4. CARBONATE OF SODA.

Caustic soda, bicarbonate of soda, and salts of soda with organic acids, also nitrate of soda and chloride of sodium.

In the borate of soda the alkali is estimated best as sulphate of soda (§ 136); in the phosphate as chloride of sodium, nitrate, or carbonate of soda (§ 134).

Salts of soda with organic acids are determined either, like the corresponding potassa compounds, as chloride of sodium, or nitrate of soda; or finally, and in preference, as carbonate of soda, which latter method is not well adapted for salts of potassa.

1. *Determination as Sulphate of Soda.*

Evaporate the aqueous solution of the sulphate to dryness, and ignite and weigh the residue in a covered platinum crucible (§ 42). The process does not involve any risk of loss by decrepitation, as in the case of sulphate of potassa. If free sulphuric acid happens to be present, this is removed by means of carbonate of ammonia, in the same way as in the case of sulphate of potassa (§ 69).

With regard to the conversion of chloride of sodium, &c., into sulphate of soda, see § 97, *b*, 1. For properties of the residue, see § 69. The method is easy, and gives accurate results.

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* The washing of the residuary platinum may generally be effected by simple affusion and decantation.

2. *Determination as Nitrate of Soda.*

Same method as described in 1. The rules given and the observations made in § 97, *b*, 2, apply equally here. For properties of the residue, see § 69.

3. *Determination as Chloride of Sodium.*

Same method as described in 1. The rules given and the observations made in § 97, *b*, 3, apply equally here. For properties of the residue, see § 69.

The methods of converting the sulphate, chromate, chlorate, and silicate of soda, into chloride of sodium, will be found in Part II. of this section, under the respective heads of the acids which these salts contain.

4. *Determination as Carbonate of Soda.*

Evaporate the aqueous solution, ignite the residue, and weigh. The results are perfectly accurate. For properties of the residue, see § 69.

Caustic soda is converted into the carbonate by adding to its aqueous solution carbonate of ammonia in excess, evaporating at a gentle heat, and igniting the residue.

Bicarbonate of soda, if in the dry state, is converted into the carbonate by ignition. The heat must be very gradually increased, and the crucible kept well covered; if in aqueous solution, it is evaporated to dryness, in a capacious silver or platinum dish, and the residue ignited.

Salts of soda with organic acids are converted into the carbonate by ignition in a covered platinum crucible, from which the lid is removed after a time. The heat must be increased very gradually. When the mass has ceased to swell, the crucible is placed obliquely, with the lid leaning against it (see § 52, Fig. 60), and a dull red heat applied until the carbon is consumed as far as practicable. The contents of the crucible are then warmed with water, and the fluid is filtered off from the residuary carbon, which is carefully washed. The filtrate and rinsings are evaporated to dryness; the residue is ignited and weighed. If the quantity of carbon is very trifling (a few milligrammes), the crucible may be weighed at once with its contents after the process of ignition, the weight of the carbon being subsequently deducted from the resulting number. For this purpose the carbon is collected on a small weighed filter, carefully dried with the latter, and weighed. Both methods give accurate results, provided, of course, they be properly and carefully executed. A direct experiment (No. 56), performed after the latter method, gave 99·7 instead of 100 parts of soda. If, however, the quantity of carbon exceeds from 10 to 20 milligrammes, the former method is preferable, being less liable to error in weighing.

Nitrate of soda, or chloride of sodium, may be converted into carbonate, by adding to the aqueous solution of the nitrate or chloride perfectly pure oxalic acid in moderate excess, and evaporating several times to dryness, with repeated renewal of the water. All the nitric acid of the nitrate of soda escapes in this process, partly decomposed, partly undecomposed; and equally so all the hydrochloric acid in the case of chloride of sodium. If the residue is now ignited until the excess of oxalic acid is removed, carbonate of soda is left.

§ 99.

3. OXIDE OF AMMONIUM (*Ammonia*).

a. Solution.

Ammonia is soluble in water, as are all its salts with those acids which claim our attention here. It is not always necessary, however, to dissolve the ammoniacal salts for the purpose of determining the amount of ammonia contained in them.

b. Determination.

Ammonia is weighed either in the form of *chloride of ammonium*, or in that of *bichloride of platinum and chloride of ammonium*. Into these forms it may be converted either *directly* or *indirectly*, *i.e.*, after previous expulsion as ammonia, and re-combination with an acid. Ammonia is also frequently determined by volumetrical analysis, or its quantity is inferred, though rarely, from the volume of nitrogen (§ 70).

We convert directly into

1. CHLORIDE OF AMMONIUM.

Ammoniacal gas and ammonia in aqueous solution, and also ammoniacal salts with weak volatile acids (carbonate of ammonia, sulphide of ammonium, &c.).

2. BICHLORIDE OF PLATINUM AND CHLORIDE OF AMMONIUM.

Ammoniacal salts with acids soluble in alcohol, such as sulphate of ammonia, phosphate of ammonia, &c.

3. The methods based on the EXPULSION OF THE AMMONIA from its compounds, and also that of inferring the amount of ammonia from the volume of nitrogen, are equally applicable to all ammoniacal salts.

The expulsion of ammonia in the dry way, by ignition with soda-lime, and the estimation of that alkali from the volume of nitrogen, being effected in the same manner as the estimation of the nitrogen in organic compounds, I refer the student on this subject to the subject on elementary organic analysis. Here I shall only give the methods based upon the expulsion of ammonia in the humid way. For the alkalimetrical estimation of free ammonia, see §§ 219 and 220.

1. *Determination as Chloride of Ammonium.*

Evaporate the aqueous solution of the chloride of ammonium on the water-bath, and dry the residue at 212° F., until the weight remains constant (§ 42). The results are accurate. The volatilization of the chloride is very trifling. A direct experiment (No. 14) gave 99·94 for 100 parts of ammonia (see the experiment, No. 14). The presence of free hydrochloric acid makes no difference; the conversion of caustic ammonia into chloride of ammonium may accordingly be effected by supersaturating with hydrochloric acid. The same applies to the conversion of the carbonate, with this addition only, that the process of supersaturation, and also that of heating to expulsion, must be conducted in an obliquely-placed flask or retort. In the analysis of sulphide of ammonium we proceed in the same way, taking care simply, after the expulsion of the sulphuretted hydrogen, and before proceeding to evaporate, to filter off the sulphur which may have separated.

2. *Determination as Bichloride of Platinum and Chloride of Ammonium.*

a. Ammoniacal salts with volatile acids.

Same method as described in § 97, *b*, 4, *a* (bichloride of platinum and chloride of potassium).

β. Ammoniacal salts with non-volatile acids.

Same method as described § 97, *b*, 4, *β* (bichloride of platinum and chloride of potassium). The results obtained by these methods are accurate.

If you wish to control the results,* ignite the double chloride, wrapped up in the filter, in a covered crucible, and calculate the amount of ammonia from that of the residuary platinum. The results must agree. The heat must be increased very gradually.† Want of due caution in this respect is apt to lead to loss, from particles of the double salt being carried away with the chloride of ammonium. Very small quantities of bichloride of platinum and chloride of ammonium are collected on an unweighed filter, dried, and at once reduced to platinum by ignition.‡

3. *Estimation by Expulsion of the Ammonia in the Humid Way.*

This method, which is applicable in all cases, may be effected in two different ways, viz.—

a. EXPULSION OF THE AMMONIA BY DISTILLING THE AMMONIACAL COMPOUND WITH SOLUTION OF POTASSA, OR SODA, OR MILK OF LIME.—Applicable in all cases where no nitrogenous organic matters from which ammonia might be evolved upon boiling with solution of potassa, etc., is present with the ammonia salts.

Weigh the substance under examination in a small glass tube, 3 centimetres long and 1 wide, and put the tube, with the substance in it, into a flask containing a suitable quantity of moderately concentrated solution of potassa or soda, or milk of lime, from which every trace of ammonia has been removed by protracted ebullition, but which has been allowed to get thoroughly cold again; place the flask in a slanting position on wire-gauze, and immediately connect it by means of a glass-tube bent at an obtuse angle, with the glass-tube of a small cooling apparatus. Connect the lower end of this tube, by means of a tight-fitting perforated cork, with a sufficiently large tubulated receiver, with a double-limbed tube fitted to it, leading from the tubulature into a small flask.

If you wish to *determine by the volumetrical method the quantity of ammonia expelled*, introduce the larger portion of a measured quantity of standard solution of oxalic acid, or standard solution of sulphuric acid (§ 215), into the receiver, the remainder into the little flask; add to the portion of fluid in the latter a little water, and color the liquids in the receiver and flask red with 1 or 2 cubic centimetres of litmus tincture. The cooling tube must not dip into the fluid in the receiver, but the double-limbed tube must reach nearly to the bottom of the little flask, to make sure that the escaping gas-bubbles pass through the fluid in the flask. The quantity of acid in receiver and flask must be more than sufficient to fix the whole of the ammonia expelled.

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* If the bichloride of platinum and chloride of ammonium is pure, which may be known by its color and general appearance, this control may be dispensed with.

† The best way is to continue the application of a moderate heat for a long time, then to remove the lid, place the crucible obliquely, with the lid leaning against it, and burn the charred filter at a gradually increased heat (*H. Rose*).

‡ In a series of experiments to get the platinum from pure and perfectly anhydrous ammonio-bichloride of platinum, by very cautious ignition, *M. Lucius*, one of my pupils, obtained from 44·1 to 44·3 per cent. of the metal, instead of 44·36.

When the apparatus is fully arranged, and you have ascertained that all the joints are perfectly tight, heat the contents of the flask to gentle ebullition, and continue the application of the same degree of heat until the drops, falling from the cooling-tube into the receiver, have for some time altogether ceased to impart the least tint of blue to the portion of the fluid in immediate contact with them. Remove now the source of heat, allow the contents of the small flask to recede into the receiver, and inject repeatedly with the washing-bottle, small quantities of water into the flask, allowing the fluid each time to recede into the receiver. Remove now, finally, the receiver, determine, with a standard solution of soda, the quantity of acid still free, which, by simple subtraction, will give the amount of acid which has combined with the ammonia; and from this you may now calculate the amount of the latter (§ 220).

If you wish to *determine by the gravimetrical method the quantity of ammonia expelled*, receive the ammonia evolved in a quantity of hydrochloric acid more than sufficient to fix the whole of it, and determine the chloride of ammonium formed, either by simple evaporation, after the directions of 1, or as ammonio-bichloride of platinum, after the directions of 2.

b. EXPULSION OF THE AMMONIA BY MILK OF LIME, WITHOUT APPLICATION OF HEAT.—This method, recommended by *Schlösing*, is based upon the fact that an aqueous solution containing free ammonia gives off the latter completely, and in a comparatively short time, when exposed in a shallow vessel to the air, at the common temperature. It finds application in cases where the presence of organic nitrogenous substances, decomposable by boiling alkalies, forbids the use of the method described in 3, *a*; thus, for instance, in the quantitative estimation of the ammonia in urine, manures, &c.

The fluid containing the ammonia, the volume of which must not exceed 35 cubic centimetres, is introduced into a shallow vessel with low rim, and from 10 to 12 centimetres in diameter; this vessel is put on a plate filled with mercury. A triangle, made of a massive glass rod, is placed upon the vessel which contains the solution of the ammoniacal salt, and a saucer or shallow basin with 10 cubic centimetres of the standard solution of oxalic or sulphuric acid (§ 215) put on it. A beaker is now inverted over the whole. The beaker is lifted up on one side as far as is required, and a sufficient quantity of milk of lime added by means of a pipette (which should not be drawn out at the lower end). The beaker is then rapidly pressed down, and weighted with a stone slab. After forty-eight hours the glass is lifted up, and a slip of moist reddened litmus paper held in it; if no change of color is observable, this is a sign that the expulsion of the ammonia is complete; in the contrary case, the glass must be replaced. Instead of the beaker and plate with mercury, a bell-jar, with a ground and greased rim, placed air-tight on a smooth glass plate, may be used. A bell-jar, having at the top a tubular opening, furnished with a close-fitting glass stopper, answers the purpose best, as it permits the introduction of a slip of red litmus paper suspended from a thread; thus enabling the operator to see whether the combination of the ammonia with the acid is completed, without the necessity of removing the bell-jar. According to *Schlösing*, forty-eight hours are always sufficient to expel 0·1 to 1 gramme of ammonia from 25 to 35 cubic centimetres of solution. However, I can admit this statement only as regards quantities up to 0·3 gramme; quantities above this often require much longer time. I, therefore, always prefer operating with quantities of substance containing no more than 0·3 gramme of ammonia at the most.

When all the ammonia has been expelled, and has entered into combination with the acid, the quantity of acid left free is determined by means of standard solution of soda, and the amount of the ammonia calculated from the result (§ 220).

§ 100.

Supplement to the First Group.

LITHIA.

In the absence of other bases, lithia may, like potassa and soda, be converted into anhydrous SULPHATE, and weighed in that form ($Li\,O, S\,O_3$). As lithia forms no acid sulphate, the excess of sulphuric acid may be readily removed by simple ignition. CARBONATE OF LITHIA also, which is difficultly soluble in water, and fuses at a red heat without suffering decomposition, is well suited for weighing; whilst chloride of lithium, which deliquesces in the air, and is by ignition in moist air converted into hydrochloric acid and lithia, is not suited for the quantitative estimation of lithia.

In presence of other alkalies, lithia is converted into BASIC PHOSPHATE OF LITHIA ($3\,Li\,O, P\,O_5$), and weighed in that form. This is effected by the following process: add to the solution a sufficient quantity of phosphate of soda (which must be perfectly free from phosphate of the alkaline earths), and as much dilute solution of soda as is required to keep the reaction alkaline to the end of the subsequent process, and evaporate the mixture to dryness; pour water over the residue, in sufficient quantity to dissolve the soluble salts with the aid of a gentle heat, add an equal volume of solution of ammonia, digest at a gentle heat, filter after twelve hours, and wash the precipitate with a mixture of equal volumes of water and solution of ammonia. Evaporate the filtrate and first washings to dryness, and treat the residue in the same way as before. If some more phosphate of lithia is thereby obtained, add this to the principal quantity. The process gives, on an average, 99·61 for 100 parts of lithia.

If the quantity of lithia present is relatively very small, the larger portion of the potassa or soda compounds should first be removed by addition of absolute alcohol to the most highly concentrated solution of the salts (chlorides, bromides, iodides, or nitrates, but not sulphates); since this, by lessening the amount of water required to effect the separation of the phosphate of lithia from the soluble salts, will prevent loss of lithia (*W. Mayer*).*

The precipitated basic phosphate of lithia has the formula $3\,Li\,O, P\,O_5 + aq.$ It dissolves in 2539 parts of pure, and 3920 parts of ammoniated water; at 212° F., it completely loses its water; if pure, it does not cake at a moderate red heat (*Mayer*).

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* "Annal. der Chem. u. Pharm.," 98, 193, where *Mayer* has also demonstrated the non-existence of a phosphate of soda and lithia of fixed composition (*Berzelius*), or of varying composition (*Rammelsberg*).

SECOND GROUP.

BARYTA—STRONTIA—LIME—MAGNESIA.

§ 101.

1. Baryta.

a. Solution.

Caustic baryta is soluble in water, as are many of the salts of that alkaline earth. The salts of baryta which are insoluble in water are, with the exception of the sulphate, readily dissolved by dilute hydrochloric acid. The solution of the sulphate is effected by fusion with a mixture of carbonate of soda and potassa, &c. See § 132.

b. Determination.

Baryta is weighed either as *sulphate*, or as *carbonate* (§ 71). It is rarely converted into *silico-fluoride of barium*, and only for the purpose of separating it from strontia. Baryta in the pure state, or in form of carbonate, may also be determined by the volumetrical (alkalimetrical) method. Comp. § 223.

We may convert into

1. Sulphate of Baryta.

a. By Precipitation.	*b. By Evaporation.*
All compounds of baryta without exception.	All compounds of baryta with volatile acids, if no other non-volatile body is present.

2. Carbonate of Baryta.

α. All salts of baryta soluble in water.

β. Salts of baryta with organic acids.

The method of precipitating baryta in the form of sulphate is the most frequently employed, being the best adapted also for the separation of baryta from other bases. The method of evaporating (1, *b*) yields accurate results, and is very convenient in cases where we have to deal with small portions of fluid only. The conversion into the carbonate in the humid way is resorted to only in cases where the conversion into the sulphate is inadmissible or unadvisable.

1. *Determination as Sulphate of Baryta.*

a. By Precipitation.

Heat the moderately dilute solution of baryta, which must not contain too much free acid, and must, therefore, if necessary, first be freed therefrom by evaporation or addition of carbonate of soda, in a platinum or porcelain dish, or in a glass vessel, to incipient ebullition, add dilute sulphuric acid, as long as a precipitate forms, keep the mixture for some time at a temperature very near the boiling point, and allow the precipitate a few minutes to subside; decant the almost clear supernatant fluid on a filter, boil the precipitate a second, third, and fourth time with water, then transfer it also to the filter, and wash with boiling water, until the filtrate is no longer rendered turbid by chloride of barium. Dry the precipitate, and treat it as directed in § 53. If the precipitate has been properly washed in the manner here directed, it is perfectly pure, and gives up no chloride of barium to acetic acid, even if boiling, nor any appreciable trace of it, to boiling nitric acid, though the solution had contained that salt.*

b. By Evaporation.

Add to the solution, in a weighed platinum dish, pure sulphuric acid very slightly in excess, and evaporate on the water-bath; expel the excess of sulphuric acid by cautious application of heat, and ignite the residue.

For the properties of sulphate of baryta, see § 71.

Both methods, if properly and carefully executed, give almost absolutely accurate results.

2. *Determination as Carbonate of Baryta.*

a. In Solutions.

Mix the moderately dilute solution of the baryta salt, in a beaker with ammonia, add carbonate of ammonia in moderate excess, and let the mixture stand several hours in a warm place. Filter, wash the precipitate with water mixed with a little ammonia, dry, and ignite (§ 53).

For the properties of the precipitate, see § 71. This method involves a trifling loss of substance, as the carbonate of baryta is not absolutely insoluble in water. The direct experiment, No. 57, gave 99·79 instead of 100 parts of baryta.

If the solution contains a notable quantity of ammoniacal salts, the loss incurred is much more considerable, since the presence of such salts greatly increases the solubility of the carbonate of baryta.

b. In Salts of Baryta with Organic Acids.

Heat the salt slowly in a covered platinum crucible, until no more fumes are evolved; place the crucible obliquely, with the lid leaning against it, and heat to redness, until the whole of the carbon is consumed, and the residue presents a perfectly white appearance; moisten the residue with a concentrated solution of carbonate of ammonia, evaporate, ignite gently, and weigh. The results obtained by this method are quite satisfactory. A direct experiment, No. 58, gave 99·61 instead of 100 parts of baryta. The loss of substance, which almost invariably attends this method, is owing to particles of the salt being carried away with the fumes evolved upon ignition, and is accordingly the less considerable, the more slowly and gradually the heat is increased. Omission of the moistening the residue with carbonate of ammonia would involve a further loss of substance, as the ignition of carbonate of baryta in contact with carbon is attended with formation of some caustic baryta, and evolution of carbonic oxide gas.

§ 102.

2. STRONTIA.

a. Solution.

See the preceding paragraph (§ 101, *a.*—Solution of baryta), the directions there given applying equally here.

b. Determination.

Strontia is weighed either as *sulphate* or as *carbonate of strontia* (§ 72). Strontia in the pure state, or in form of carbonate, may be determined also by the volumetrical (alkalimetrical) method. Comp. § 223.

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* I mention this in reference to *Siegle's* statement in the "Journal f. prakt. Chem.," 69, 142, that acetic acid and nitric acid will still extract small quantities of chloride of barium from sulphate of baryta, formed in presence of an excess of sulphuric acid, and thoroughly washed with water.

We may convert into

1. SULPHATE OF STRONTIA.

a. By Precipitation.

All compounds of strontia without exception.

b. By Evaporation.

All salts of strontia with volatile acids, if no other non-volatile body is present.

2. CARBONATE OF STRONTIA.

α. All compounds of strontia soluble in water.

β. Salts of strontia with organic acids.

The method based on the precipitation of strontia with sulphuric acid yields accurate results only in cases where the fluid from which the strontia is to be precipitated may be mixed, without injury, with alcohol. Where this cannot be done, and where the method based on the evaporation of the solution of strontia with sulphuric acid is equally inapplicable, the conversion into the carbonate ought to be resorted to in preference, if admissible, in the case of soluble compounds of strontia and of salts of strontia with organic acids.

1. *Determination as Sulphate of Strontia.*

a. By Precipitation.

Mix the solution of the salt of strontia (which must not be too dilute, nor contain much free hydrochloric or nitric acid), with dilute sulphuric acid in excess, in a beaker, and add, at least, an equal volume of alcohol; let the mixture stand a few hours, and filter; wash the precipitate with dilute spirit of wine, dry, ignite, and weigh the residue (§ 53).

If the circumstances of the case contraindicate the use of alcohol, the fluid must be precipitated in a tolerably concentrated state, allowed to stand in the cold for at least twenty-four hours, filtered, and the precipitate washed with cold water, until the last rinsings manifest no longer an acid reaction, and leave no perceptible residue upon evaporation. If traces of free sulphuric acid remain adhering to the filter, the latter turns black on drying, and crumbles to pieces; too long protracted washing of the precipitate, on the other hand, tends to increase the loss of substance inseparable from the application of this method in cases where the use of alcohol is inadmissible.

Care must be taken that the precipitate be thoroughly dry, before proceeding to ignite it; otherwise it will be apt to throw off fine particles during the latter process. The filter, which is to be burnt on the lid of the crucible, must be as clean as possible, or some loss of substance will be incurred; as may be clearly seen from the depth of the carmine tint of the flame with which the filter burns if the precipitate has not been properly removed.

For the properties of the precipitate, see § 72. This method gives very accurate results in cases where the addition of alcohol to the solution is admissible; but where we have to deal with a simple aqueous solution, a rather considerable loss is unavoidable, as sulphate of strontia is not absolutely insoluble in water. The direct experiments, No. 59, gave only 98·12 and 98·02 instead of 100 parts of strontia. However, the error may, in a great measure, be rectified, by calculating the amount of sulphate of strontia dissolved in the filtrate and the rinsing water, basing the calculation upon the known degree of solubility of sulphate of strontia in pure and acidified water. See Experiment No. 60, which, with this correction, gave 99·77 instead of 100 parts of strontia.

b. By Evaporation.

The same method as described § 101, 1, *b*.

2. *Determination as Carbonate of Strontia.*

a. In Solutions,

The same method as described § 101, 2, *a*. For the properties of the precipitate, see § 72. The method gives very accurate results, as carbonate of strontia is nearly absolutely insoluble in water containing ammonia and carbonate of ammonia. A direct experiment, No. 60, gave 99·82 instead of 100 parts of strontia. Presence of ammoniacal salts exercises here a less adverse influence, than in the precipitation of carbonate of baryta.

b. In Salts with Organic Matter.

The same method as described § 101, 2, *b*. The remarks made there, respecting the accuracy of the results, apply equally here.

§ 103.

3. LIME.

a. Solution.

See § 101 *a*.—Solution of baryta. Fluoride of calcium is, by means of sulphuric acid, converted into sulphate of lime, and the latter again, if necessary, decomposed by boiling or fluxing with an alkaline carbonate (§ 132).

b. Determination.

Lime is weighed either as *sulphate*, or as *carbonate of lime* (§ 73).

Small quantities of lime are also occasionally reduced to the caustic state, instead of being converted into carbonate. Lime in the pure state, or in form of carbonate, may be determined also by the volumetrical (alkalimetrical) method. Comp. § 223.

We may convert into

1. SULPHATE OF LIME.

a. By Precipitation.

All salts of lime with acids soluble in alcohol, provided no other substance insoluble in alcohol be present.

b. By Evaporation.

All salts of lime with volatile acids, provided no non-volatile body be present.

2. CARBONATE OF LIME.

a. By Precipitation with Carbonate of Ammonia.

All salts of lime soluble in water.

b. By Precipitation with Oxalate of Ammonia.

All salts of lime soluble in water or in hydrochloric acid.

c. By Ignition.

Salts of lime with organic acids.

Of these several methods, 2, *b*. (precipitation with oxalate of ammonia) is the one most frequently resorted to. This, and the method 1, *b*, give the most accurate results. The method, 1, *a*, is usually resorted to only to effect the separation of lime from other bases; 2, *a*, generally only to effect the separation of lime together with other alkaline earths from the alkalies.

1. *Determination as Sulphate of Lime.*

a. By Precipitation.

Mix the solution of lime in a beaker, with dilute sulphuric acid in excess, and add twice the volume of alcohol; let the mixture stand twelve hours, filter, and *thoroughly* wash the precipitate with spirit of wine, dry, and ignite moderately (§ 53). For the properties of the precipitate, see § 73. The results are very accurate. A direct experiment, No. 62, gave 99·64 instead of 100 parts of lime.

b. By Evaporation.

The same method as described § 101, 1, *b*. See also § 103, 2, *b*, *a*.

2. *Determination as Carbonate of Lime.*

a. By Precipitation with Carbonate of Ammonia.

The same method as described § 101, 2, *a*. The precipitate must be exposed only to a very gentle red heat, but this must be continued for some time. For the properties of the precipitate, see § 73.

This method gives very accurate results, the loss of substance incurred being hardly worth mentioning.

If the solution contains chloride of ammonium or similar ammoniacal salts in considerable proportion, the loss of substance incurred is far greater. The same is the case if the precipitate is washed with pure instead of ammoniacal water. A direct experiment, No. 63, in which pure water was used, gave 99·17 instead of 100 parts of lime.

b. By Precipitation with Oxalate of Ammonia.

a. The Lime Salt is soluble in Water.

Dissolve the salt in hot water, in a beaker; add oxalate of ammonia in moderate excess, and then ammonia sufficient to impart an ammoniacal smell to the fluid; cover the glass, and let it stand in a warm place until the precipitate has completely subsided, which will require twelve hours, at least. Pour the clear fluid gently and cautiously, so as to leave the precipitate undisturbed, on a proper filter. As soon as the fluid has passed through, transfer the precipitate also to the filter, by rinsing with hot water, taking care, after the addition of every fresh portion, to wait until the fluid has completely passed through the filter. Small particles of the precipitate, adhering more firmly to the glass, are removed with a feather. If this fails to effect their complete removal, they should be dissolved, in a small vessel, in a few drops of highly dilute hydrochloric acid, ammonia added to the solution, and the oxalate obtained added to the first precipitate. Deviations from the rules laid down here will generally give rise to the passing of a turbid fluid through the filter. After having washed the precipitate, dry it on the filter in the funnel, and transfer the dry precipitate to a platinum crucible, taking care to scrape the filter as clean as practicable; burn the filter on a piece of platinum wire, letting the ash drop into the hollow of the lid; put the latter, now inverted, on the crucible, to prevent the filter ash mixing with the precipitate; apply a gentle heat, and increase this gradually, until the bottom of the crucible is heated to very faint redness. Keep it at that temperature from ten to fifteen minutes, then let it cool, and weigh. After this, moisten the contents of the crucible, which must be perfectly white, or barely show the least tinge of gray, with a little water, and test this after a time with a slip of turmeric paper. If the color of the test paper remains unaltered, the process may be considered at an end, and the result taken as correct; but should the paper turn brown—a sign that the heat applied was too intense—rinse off the fluid adhering to the paper with a little water into a crucible, throw in a small lump of pure carbonate of ammonia, evaporate to dryness (best in the water-bath), heat to very faint redness, and weigh the residue. If the weight shows an increase over that of the first residue, repeat the same operation until the weight remains constant. This method, if properly and carefully performed, in strict accordance with the directions, gives nearly absolutely accurate results; and if the application of heat is properly managed, there is no need of the tedious supplementary operation recommended here—evaporation with carbonate of ammonia. A direct experiment, No. 67, gave 99·99 instead of 100 parts of lime.

For the properties of the precipitate and residue, see § 73.

If the quantity of oxalate of lime obtained is only very trifling, I prefer to convert it into the sulphate, or to reduce it to the caustic state. To effect the latter, the oxalate of lime is heated to intense redness, in a small platinum crucible, over a gas blowpipe-flame, and the operation continued long enough to effect the reduction of the oxalate to the caustic state. The conversion of the oxalate into sulphate is effected most conveniently by *Schrötter's* method, viz., ignition with pure sulphate of ammonia.

Many chemists prefer collecting the oxalate of lime upon a weighed filter, drying at 212° F., and weighing the dry precipitate. This precipitate is not, as is often erroneously supposed, $Ca\,O,\,C_2O_3$, but, $Ca\,O,\,C_2O_3 + aq.$, and must therefore be calculated as such.

This method, besides being more tedious, gives less accurate results than that based on the conversion of the oxalate into the carbonate. The direct experiment, No. 65, gave 100·45 instead of 100 parts of lime.

Instead of weighing the oxalate of lime as such, or in form of carbonate, &c., the quantity of lime present in the salt may be determined also by two different volumetrical methods.

a. *Ignite* the oxalate, converting it thus into a mixture of carbonate and caustic lime, and determine the quantity of the lime by the alkalimetrical method described in § 223; or,

b. Determine the oxalic acid in the well-washed but not yet dried oxalate of lime, by means of permanganate of potassa (§ 137), and reckon for each equivalent of oxalic acid ($C_2\,O_3$) an equivalent of lime (*Hempel*).

With proper care, both these volumetrical methods give as accurate results as those obtained by weighing. (Comp. Experiment No. 66.) They deserve to be recommended more particularly in cases where an entire series of quantitative estimations of lime has to be made. Under certain circumstances it may also prove advantageous to precipitate the lime with a measured quantity of a standard solution of oxalic acid or quadraoxalate of potassa, filter, and determine the excess of oxalic acid in the filtrate (*Kraut.* "Chem. Centralblatt," 1856, 316).

β. The Salt is insoluble in Water.

Dissolve the salt in dilute hydrochloric acid. If the acid combined with the lime is of a nature to escape in this operation (*e. g.*, carbonic acid), or to admit of its separation by evaporation (*e. g.*, silicic acid), proceed, after the removal of the acid, as directed in *a*. But if the acid is of more stable nature (*e. g.*, phosphoric acid), neutralize the free acid present with ammonia until a precipitate begins to form, re-dissolve this again with a drop of hydrochloric acid, add oxalate of ammonia in excess, and finally acetate of soda; allow the precipitate to subside, and proceed for the remainder of the operation as directed in *a*. In this process the free hydrochloric acid present combines with the ammonia and soda of the oxalate and acetate, liberating a corresponding quantity of oxalic acid and acetic acid, in which acids oxalate of lime is nearly insoluble. The method yields pretty accurate results. A direct experiment, No. 67, gave 99·78 instead of 100 parts of lime.

c. By Ignition.

The same method as described § 101, 2, *b* (baryta). The residue remaining upon evaporation with carbonate of ammonia (which operation it is advisable to perform twice) must be ignited very gently. The remarks made in § 101, 2, *b*, in reference to the accuracy of the results, apply equally here. By way of control, the carbonate of lime may be converted into sulphate or reduced to the caustic state. See *b*, *a*.

§ 104.

4. Magnesia.

a. Solution.

Many of the compounds of magnesia are soluble in water; those which are insoluble in that menstruum dissolve in hydrochloric acid, with the exception of some silicates and aluminates.

b. Determination.

Magnesia is weighed either as *sulphate of magnesia*, or as *pyrophosphate*, or as *pure magnesia*. In the pure state, or in form of carbonate, it may be determined also by the alkalimetrical method described in § 223.

We may convert into

1. Sulphate of Magnesia.

a. Directly.	*b. Indirectly.*
All compounds of magnesia with volatile acids, provided no other non-volatile substance be present.	All compounds of magnesia soluble in water, and also those which, insoluble in that menstruum, dissolve in hydrochloric acid, with separation of their acid (provided no ammoniacal salts be present).

2. Pyrophosphate of Magnesia.

All compounds of magnesia without exception

3. Pure Magnesia.

a. Salts of magnesia with organic acids, or with readily volatile inorganic oxygen acids.

b. Chloride of magnesium, and the compounds of magnesia convertible into that salt.

The direct determination as sulphate of magnesia is highly recommended in all cases where it is applicable. The indirect conversion into the sulphate serves only to separate magnesia from certain bases, and is hardly ever had recourse to where it can possibly be avoided. The method based on the conversion of the magnesia compound into the pyrophosphate is most generally resorted to; especially also to effect the separation of magnesia from other bases. The method based on the conversion of chloride of magnesium into pure magnesia is usually resorted to only to effect the separation of magnesia from the fixed alkalies. Compounds of magnesia with phosphoric acid are analysed as § 134 directs.

1. *Determination as Sulphate of Magnesia.*

a. Direct Determination.

Add to the solution of magnesia a more than sufficient amount of dilute pure sulphuric acid to combine with the whole of the magnesia present, evaporate the mixture to dryness, in a weighed platinum dish, on the water-bath; heat cautiously at first, then, after putting on the lid, more strongly, until the excess of sulphuric acid is completely expelled; heat the residue now over the lamp for some time to gentle redness; let it cool, and weigh. Should no fumes of hydrated sulphuric acid escape upon the application of a stronger heat, this may be looked upon as a sure sign that the sulphuric acid has not been added in sufficient quantity, in which case the mixture is allowed to cool, and a fresh portion of sulphuric acid added. The method yields very accurate results. Care must be taken not to use a very large quantity of sulphuric acid, since this would tend to protract the process unnecessarily; the residue must be exposed to a moderate red heat only, and weighed, as soon as cold. For the properties of the residue, see § 74.

b. Indirect Determination.

The solution of magnesia is heated, in a flask, to 212° F., and clear saturated water of baryta added in excess; the temperature is maintained near the boiling point for some time; the fluid is then filtered off from the precipitate, and the latter carefully washed with boiling water, and subsequently dissolved upon the filter, with somewhat dilute warm hydrochloric acid; the filter is also carefully washed, and the further operation conducted as directed in *a*. Should a precipitate of sulphate of baryta form upon the addition of the sulphuric acid, this may be considered a sign that the carbonic acid of the air has not been sufficiently excluded from contact with the water of baryta during the operation. In that case, we may either allow this precipitate to subside, filter, and evaporate the filtrate; or we may evaporate at once, weigh the residue, dissolve in water containing hydrochloric acid, filter the solution off from the undissolved sulphate of baryta, ascertain the weight of the latter (§ 101, 1, *a*), and subtract this from the original residue.

The results obtained by this method fall somewhat short of 100, since hydrated magnesia is not quite insoluble in water. The method is, moreover, rather too complicated to yield perfectly accurate results.

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2. *Determination as Pyrophosphate of Magnesia.*

The solution of the salt of magnesia is mixed, in a beaker, with chloride of ammonium, and ammonia added in slight excess. Should a precipitate form upon the addition of ammonia, this may be considered a sign that a sufficient amount of chloride of ammonium has not been used; a fresh amount of that salt must consequently be added, sufficient to effect the re-solution of the precipitate formed. The fluid is then mixed with a solution of phosphate of soda in excess, and the mixture stirred with a glass rod, taking care to avoid touching the sides of the beaker with the stirring-rod; otherwise particles of the precipitate are apt to adhere so firmly to the rubbed parts of the beaker, that it will be found difficult to remove them; the beaker is then well covered, and allowed to stand at rest for twelve hours, in a moderately warm place; after that time the fluid is filtered, and the precipitate collected on the filter, the last particles of it being rinsed out of the glass with a portion of the filtrate, with the aid of a feather; when the fluid has completely passed through, the precipitate is carefully washed with a mixture of 3 parts of water, and 1 part of solution of ammonia of 0·96 specific gravity, the operation being continued until a drop of the fluid passing through the filter no longer leaves a residue when evaporated upon a platinum knife.

The precipitate is now thoroughly dried, and then transferred to a platinum crucible (§ 53); the latter, with the lid on, is exposed for some time to a very gentle heat, which is finally increased to intense redness. The filter, scraped as clean as practicable, is incinerated in a spiral coil of platinum wire, and the ash transferred to the crucible, which is then once more exposed to a red heat, allowed to cool, and weighed.

For the properties of the precipitate and residue, see § 74.

This method, if properly executed, yields most accurate results.

Direct experiments, No. 66 *a* and *b*, gave respectively 100·09 and 99·97 instead of 100 parts of magnesia.

3. *Determination as pure Magnesia.*

a. In Salts of Magnesia with Organic or Volatile Inorganic Acids.

The salt of magnesia is gently heated in a covered platinum crucible, increasing the temperature gradually, until no more fumes escape; the lid is then removed, and the crucible placed in an oblique position, with the lid leaning against it. A red heat is now applied, until the residue presents a perfectly white appearance. For the properties of the residue, see § 74. The method gives pretty accurate results, provided the application of heat be managed slowly and gradually. Some loss of substance is usually sustained, owing to traces of the salt being carried off with the empyreumatic products. Salts of magnesia with readily volatile oxygen acids (carbonic acid, nitric acid), may be reduced to magnesia in a similar way, by simple ignition. Even sulphate of magnesia is completely reduced to the caustic state when exposed, in a platinum crucible, to the heat of the gas blowpipe-flame (*Sonnenschein*). As regards small quantities of sulphate of magnesia, I can fully confirm this statement.

b. Conversion of Chloride of Magnesium into pure Magnesia.

The concentrated solution of chloride of magnesium is mixed in a porcelain crucible, with levigated pure oxide of mercury, added in proportion more than sufficient to convert by its oxygen the whole of the magnesium present into magnesia. The mixture is evaporated on the water-bath, and the residue thoroughly dried; the crucible is now covered, and exposed to a red heat, until the chloride of mercury formed is expelled, together with the excess of oxide of mercury. The operator should carefully guard against inhaling the fumes evolved. The residue of magnesia is either weighed at once in the crucible, or if the operation had for its object the separation of the earth from the alkalies, it is collected upon a filter, washed with hot water, dried, and ignited (§ 53). Compare also § 153, B, 4 (17–21), where some other methods are given to effect the same purpose.

THIRD GROUP OF THE BASES.

ALUMINA—SESQUIOXIDE OF CHROMIUM—(TITANIC ACID).

§ 105.

1. Alumina.

a. Solution.

Those of the compounds of alumina which are insoluble in water, dissolve, almost without exception, in hydrochloric acid. Native crystallized alumina (sapphire, ruby, corundum, &c.), and many native alumina compounds, and also artificially produced alumina, after intense ignition, require fluxing with carbonate of soda, caustic potassa, or hydrate of baryta, as a preliminary step to their solution in hydrochloric acid. Many alumina compounds which resist the action of concentrated hydrochloric acid, may be decomposed by protracted treatment with concentrated sulphuric acid, or by fusion with bisulphate of potassa; *e.g.* common clay.

b. Determination.

Alumina is invariably weighed in the pure state (§ 75). The several compounds of alumina are converted into pure alumina, either by precipitation as hydrate of alumina, and subsequent ignition, or by simple ignition.

We may convert into

PURE ALUMINA.

a. By Precipitation.	*b. By Heating or Ignition.*
All compounds of alumina soluble in water, and those which, insoluble in that menstruum, dissolve in hydrochloric acid, with separation of their acid.	*α*. All salts of alumina with readily volatile acids (sesquichloride of aluminium, nitrate of alumina, &c.) *β*. All salts of alumina with organic acids.

The methods *b*, *α*, and *β*, are applicable only in cases where no other fixed substances are present. The method of estimating alumina in its combination with phosphoric acid, boracic acid, silicic acid, and chromic acid, will be found in Part II. of this section, under the respective heads of these several acids.

Determination as pure Alumina.

a. By Precipitation.

Mix the moderately dilute hot solution of alumina, in a beaker, with a pretty considerable quantity of chloride of ammonium, if that salt is not already present; add ammonia *slightly* in excess, and let the mixture stand for 12 hours in a warm place; then decant the clear supernatant fluid on to a filter, taking care not to disturb the precipitate; pour boiling water on the latter in the beaker, stir, let the saline particles subside, decant again, and repeat this operation of washing by decantation a second and a third time; transfer the precipitate now to the filter, wash once more with boiling water, dry thoroughly, ignite (§ 52), and weigh. The heat applied should be very gentle at first, and the crucible kept well covered, to guard against the risk of loss of substance from spurting, which is always to be apprehended if the precipitate is not *thoroughly* dry; towards the end of the process the heat should be raised to intense redness. In the case of *sulphate* of alumina the foregoing process is apt to leave some sulphuric acid in the precipitate, which, of course, vitiates the result. To ensure the removal of this sulphuric acid, the precipitate should be exposed for a quarter of an hour to the heat of the gas blow-pipe flame. If there are difficulties in the way, preventing this proceeding, the precipitate, either simply washed or moderately ignited, must be re-dissolved in hydrochloric acid (which requires protracted warming with strong acid), and then precipitate again with ammonia; or the sulphate must first be converted into nitrate by decomposing it with nitrate of oxide of lead, added in very slight excess, the excess of lead removed by means of hydrosulphuric acid, and the further process conducted according to the directions of *a* or *b*. For the properties of hydrate of alumina and ignited alumina, see § 75. The method, if properly executed, gives very accurate results. But if a considerable excess of ammonia is used, more particularly when no ammoniacal salts are present, and when the addition of chloride of ammonium has been omitted, a very considerable loss is likely to be incurred; this loss is the greater the more dilute the solution, and the shorter the time which elapses between the precipitation and decantation.

b. By direct Ignition.

α. Compounds of Alumina with volatile Acids.

aa. In the solid State.

Expose the salt (in the case of sesquichloride of aluminium, after previous addition of water), in a platinum crucible, to a red heat, gentle at first, but increased gradually to the very highest degree of intensity, until the weight remains constant. For the properties of the residue see § 75. The purity of the residue must be carefully tested. This method gives accurate results.

bb. In Solution.

Evaporate the solution to dryness on the water-bath, and proceed with the residue as directed in *aa.*

β. Compounds of Alumina with Organic Acids.

The same method as described § 104, 3. *a* (Magnesia).

§ 106.

2. SESQUIOXIDE OF CHROMIUM.

a. Solution.

Many of the compounds of sesquioxide of chromium are soluble in water. Hydrated sesquioxide of chromium, and most of the salts of sesquioxide of chromium insoluble in water, dissolve in hydrochloric acid. Ignition renders sesquioxide of chromium and many of its salts insoluble in acids; this insoluble modification must be prepared for solution in hydrochloric acid, by fluxing with 3 or 4 parts of carbonate of soda. A small quantity of sesquioxide of chromium is converted, in the process of fluxing, into chromic acid, by the action of the air; this is, however, reduced again to sesquioxide upon heating with hydrochloric acid. Addition of alcohol greatly promotes the reduction. For the solution of chrome-ironstone, see § 160.

b. Determination.

Sesquioxide of chromium may be weighed in the *pure state*, or it may be converted into *chromic acid*, and its weight calculated from the amount of the latter (see § 130). The several compounds of sesquioxide of chromium are reduced to the sesquioxide either by precipitation as hydrated sesquioxide, and subsequent ignition, or by simple ignition.

We may convert into

1. PURE SESQUIOXIDE OF CHROMIUM.

a. By Precipitation.

All compounds of sesquioxide of chromium soluble in water, and also those which, insoluble in that menstruum, dissolve in hydrochloric acid, with separation of their acid.

b. By Ignition.

α. All salts of sesquioxide of chromium with volatile oxygen acids, provided no non-volatile substances be present.

β. Salts of sesquioxide of chromium with organic acids.

2. CHROMIC ACID, or, more correctly speaking, ALKALINE CHROMATE.

Sesquioxide of chromium and all its salts.

The methods of estimating the sesquioxide of chromium in its combinations with chromic acid, phosphoric acid, boracic acid, and silicic acid, will be found in Part II. of this section, under the respective heads of these several acids.

1. *Determination as Sesquioxide of Chromium.*

a. By Precipitation.

The salt is dissolved in a beaker, and the solution, which must not be too highly concentrated, heated to 212° F. Ammonia is then added slightly in excess, and the mixture exposed to a temperature approaching boiling, until the fluid over the precipitate is perfectly colorless, presenting no longer the least shade of red; let the solid particles subside, wash three times by decantation, and lastly once more on the filter, with hot water, dry thoroughly, and ignite (§ 52). The heat in the latter process must be increased gradually, and the crucible kept covered, otherwise some loss of substance is likely to arise from spurting upon the incandescence of the sesquioxide of chromium which marks the passing of the soluble into the insoluble modification. For the properties of the precipitate and residue, see § 76. This method, if properly executed, gives very accurate results.

b. By direct Ignition.

α. Salts of Sesquioxide of Chromium with Volatile Acids.

The same method as described, § 105, *b*, *α* (Alumina).

β. Salts of Sesquioxide of Chromium with Organic Acids.

The same method as described § 104, 3, *a* (Magnesia).

2. CONVERSION OF SESQUIOXIDE OF CHROMIUM INTO CHROMIC ACID (in combination with an alkali).

(For the estimation of chromic acid, see § 130.)

The following methods have been proposed to effect the conversion of sesquioxide of chromium into an alkaline chromate.

a. The solution of the salt of sesquioxide of chromium is mixed with solution of potassa or soda in excess, until the hydrated sesquioxide, which forms at first, is redissolved. Chlorine gas is then conducted into the cold fluid until it acquires a yellowish-red tint; it is then mixed with potassa or soda in excess, and the mixture evaporated to dryness; the residue is ignited in a platinum crucible. The whole of the chlorate of potassa (or soda) formed is decomposed by this process, and the residue consists, therefore, now of an alkaline chromate and chloride of potassium (or sodium).—(*Vohl.*)

b. Hydrate of potassa is heated in a silver crucible to calm fusion; the heat is then somewhat moderated, and the perfectly dry compound of sesquioxide of chromium put in the crucible. When the sesquioxide of chromium is thoroughly moistened with the hydrated potassa, small lumps of fused chlorate of potassa are added. A lively effervescence ensues, from the escape of oxygen; at the same time the mass acquires a more and more yellow color, and finally becomes clear and transparent. Loss of substance must be carefully guarded against (*H. Schwarz*).

c. Dissolve the sesquioxide of chromium in solution of potassa or soda, add binoxide of lead in sufficient excess, and warm. The yellow fluid produced contains all the chromium as chromate of lead in the alkaline solution. Filter from the excess of binoxide of lead, add to the filtrate acetic acid to acid reaction, and determine the weight of the precipitated chromate of lead (*G. Chancel.* "Comp. rend.," 43, 927.)

§ 107.

Supplement to the Third Group.

TITANIC ACID.

Titanic acid is always weighed in the pure state; its separation is effected either by precipitation with ammonia, or from dilute acid solution, by boiling. In *precipitating* acid solutions of titanic acid with ammonia, take care to add the precipitating agent only in slight excess, let the precipitate formed, which resembles hydrate of alumina, deposit, wash, first by decantation, then completely on the filter, dry, and ignite (§ 52). If the solution contained sulphuric acid, put some carbonate of ammonia into the crucible, after the first ignition, to secure the removal of every remaining trace of that acid. Lose no time in weighing the ignited titanic acid, as this substance is slightly hygroscopic. From very dilute solutions of titanic acid in sulphuric acid, obtained by treating with cold water the mass produced by fusing titanic acid with bisulphate of potassa, the titanic acid may be separated also by *protracted boiling,* with renewal of the evaporating waters; the precipitate is washed simply with water. In the process of ignition some carbonate of ammonia is added to the dried precipitate. From dilute hydrochloric acid solutions of titanic acid, the latter separates completely only upon evaporating the fluid to dryness; and if the precipitate in that case were washed simply with water, it would pass through the filter in a milky condition; acid must, therefore, be added to the water.

Hydrate of titanic acid precipitated in the cold, washed with cold water, and dried without elevation of temperature, is completely soluble in hydrochloric acid; produced by precipitation, under different circumstances, it dissolves only incompletely in that acid. Titanic acid thrown down from dilute acid solutions by boiling, is not soluble in dilute acids. Ignited titanic acid does not dissolve even in concentrated hydrochloric acid; rather concentrated sulphuric acid will dissolve it, however, upon continued application of heat. The easiest way of effecting its solution is to fuse it for some time with bisulphate of potassa, and treat the fused mass with a large quantity of cold water. Upon fusing titanic acid with carbonate of soda, titanate of soda is formed, which, when treated with water, leaves acid titanate of soda, soluble in hydrochloric acid. Titanic acid ($Ti\ O_2$) consists of 61·2 per cent. of titanium, and 38·8 per cent. of oxygen.

Fourth Group of the Bases.

Oxide of Zinc—Protoxide of Manganese—Protoxide of Nickel—Protoxide of Cobalt—Protoxide of Iron—Sesquioxide of Iron—(Sesquioxide of Uranium).

§ 108.

1. Oxide of Zinc.

a. Solution.

Many of the salts of zinc are soluble in water. Metallic zinc, oxide of zinc, and the salts of zinc, which are insoluble in water, dissolve in hydrochloric acid.

b. Determination.

Oxide of zinc is invariably weighed as such (§ 77). The conversion of the salts of zinc into the oxide is effected either by precipitation as carbonate or sulphide of zinc, or by direct ignition. Besides these gravimetric methods, there have been proposed and adopted also several volumetric methods.

We may convert into

Oxide of Zinc.

a. By Precipitation as Carbonate of Zinc.	*b. By Precipitation as Sulphide of Zinc.*
All the salts of zinc which are soluble in water, and all those with organic volatile acids; also those salts of zinc which, insoluble in water, dissolve in hydrochloric acid, with separation of their acid.	All compounds of zinc without exception.

c. By direct Ignition.

Salts of zinc with volatile inorganic oxygen acids.

The last method is to be recommended only for carbonate of zinc and nitrate of zinc. Sulphide of zinc and sulphate of zinc require a white heat for their complete conversion into the oxide (the former with access of air). The method *b* is only resorted to in cases where *a* is inadmissible. It serves more especially to separate oxide of zinc from other bases. Salts of zinc with organic acids must not be converted into the oxide by ignition, since this process would cause the reduction of a small portion of the oxide to the metallic state, and its dissipation in vapor.

If the acids are volatile, the zinc may be determined at once according to method *a*; if, on the contrary, the acids are non-volatile, the zinc may either be precipitated as sulphide, or the salt under examination may be heated to very gentle redness, the residue extracted with nitric acid, and the solution treated according to *a* or *c*. The methods of estimating the oxide of zinc in its combinations with chromic acid, phosphoric acid, boracic acid, and silicic acid, will be found in Part II. of this section, under the heads of the several acids. The volumetrical methods are chiefly employed in technical processes. See Special Part.

Determination as Oxide of Zinc.

a. By Precipitation as Carbonate of Zinc.

Heat the moderately dilute solution of the salt of zinc under examination nearly to boiling, in a *capacious* vessel, best in a platinum dish; add, drop by drop, carbonate of soda in excess; boil a few minutes; let the solid particles subside, decant through a filter, and boil the precipitate three times with water, decanting each time; then transfer the precipitate to the filter, wash completely with hot water, dry, and ignite as directed § 53, taking care to have the filter as clean as practicable, before proceeding to incinerate it. Should the solution contain ammoniacal salts, the ebullition must be continued until, upon a fresh addition of the carbonate of soda, the escaping vapor no longer imparts a brown tint to turmeric paper. If the quantity of ammoniacal salts present is considerable, the fluid must be evaporated *boiling* to dryness. It is, therefore, in such cases more convenient to precipitate the zinc as sulphide (see *b*).

The presence of a great excess of acid in the solution of zinc must be as much as possible guarded against, that the effervescence from the escaping carbonic acid gas may not be too impetuous. The filtrate must always be tested with sulphide of ammonium, to ascertain whether the whole of the zinc has been precipitated; a *slight* precipitate will indeed *invariably* form upon the application of this test; but, if the process has been properly conducted, this is so insignificant that it may be altogether disregarded, being limited to some exceedingly slight and imponderable flakes, which moreover make their appearance only after many hours' standing (comp. § 77). If the precipitate is more considerable, however, it must be treated as directed in *b*, and the weight of the oxide of zinc obtained added to that resulting from the first process. For the properties of the precipitate and residue, see § 77. This method yields pretty accurate results, though the numbers found are in most cases a little below those given by the theoretical calculation, as the precipitation is never *absolutely* complete, and as particles of the precipitate will always and unavoidably adhere to the filter, which exposes them to the chance of reduction and volatilization during the process of ignition. On the other hand, the results show sometimes also an *excess* over the numbers theoretically calculated; this is owing to defective washing, as may be seen from the alkaline reaction which the residue manifests in such cases. It is advisable also to ascertain whether the residue will dissolve in hydrochloric acid without leaving silicic acid; this latter precaution is indispensable in cases where the precipitation has been effected in a glass vessel.

b. By Precipitation as Sulphide of Zinc.

Mix the solution of zinc with ammonia until the precipitate which first forms is redissolved; add sulphide of ammonium in moderate excess, let the precipitate subside in a warm place, and decant on to a filter, wash the precipitate three times with water containing sulphide of ammonium, each time allowing the solid particles to deposit in a warm place, and decanting; transfer the precipitate now to the filter, and complete the process of washing with water containing sulphide of ammonium; put the moist filter with the precipitate in a beaker, and pour over it concentrated hydrochloric acid slightly in excess. Put the glass now in a moderately warm place, until the solution smells no longer of sulphuretted hydrogen; dilute the fluid with a little water, filter, wash the original filter with hot water, and proceed with the solution of chloride of zinc obtained as directed in *a.*

From a solution of acetate of zinc the metal may be precipitated completely, or nearly so, with sulphuretted hydrogen gas, even in presence of an excess of acetic acid, provided always no other acid be present. The precipitated sulphide of zinc is washed with water impregnated with sulphuretted hydrogen, and, for the rest, treated exactly like the sulphide of zinc obtained by precipitation with sulphide of ammonium. (Compare Experiment No. 69.)

Small quantities of sulphide of zinc may also be converted directly into the oxide, by heating in a platinum crucible, with free access of air, to gentle redness at first, then, after some time, to most intense redness.

+ *c. By direct Ignition.*

The salt is exposed, in a covered platinum crucible, first to a gentle heat, finally to a most intense heat, until the weight of the residue remains constant.

§ 109.

2. PROTOXIDE OF MANGANESE.

a. Solution.

Many of the salts of protoxide of manganese are soluble in water. The pure protoxide, and those of its salts which are insoluble in that menstruum, dissolve in hydrochloric acid, which dissolves also the higher oxides of manganese. The solution of the higher oxides is attended with evolution of chlorine—equivalent in quantity to the amount of oxygen which the oxide under examination contains, more than the protoxide of manganese—and the fluid, after previous application of heat, is found to contain protochloride of manganese.

b. Determination.

Manganese is weighed either as *sulphate of protoxide of manganese*, or as *protosesquioxide of manganese* (§ 78). Into the latter form it is converted by precipitation as hydrated protoxide or as carbonate of protoxide, sometimes preceded, in the latter case, by precipitation as sulphide of manganese, or as binoxide of manganese; or, finally, by direct ignition.

If we have to deal with a perfectly definite higher oxide of manganese, free from other bodies evolving chlorine upon boiling with hydrochloric acid, the manganese may be determined also volumetrically and in an indirect way. For the methods of effecting this, see Special Part, under the heading "ANALYSIS OF MANGANESE ORES."

We may convert into

1. PROTOSESQUIOXIDE OF MANGANESE.

a. By Precipitation as Carbonate of Protoxide of Manganese.

All the soluble salts of manganese with inorganic acids, and all its salts with volatile organic acids; also those of its salts which, insoluble in water, dissolve in hydrochloric acid with separation of their acid.

b. By Precipitation as Hydrated Protoxide of Manganese.

All the compounds of manganese, with the exception of its salts with non-volatile organic acids.

c. By Precipitation as Sulphide of Manganese.

All compounds of manganese without exception.

d. By Separation as Binoxide of Manganese.

All compounds of manganese in a slightly acid solution, especially acetate and nitrate of protoxide of manganese.

e. By direct Ignition.

All oxygen compounds of manganese; salts of manganese with readily volatile acids, and with organic acids.

2. SULPHATE OF PROTOXIDE OF MANGANESE.

All the oxides of manganese, and likewise all its salts with volatile acids, provided no non-volatile substance be present.

The method 1, *e*, is the most simple and accurate, and is therefore preferred to all others, wherever it is admissible. The method 2, is convenient and expeditious; but its results are not absolutely accurate. The methods 1, *c* and *d*, are resorted to only in cases where the application of none of the other methods is admissible; the latter, more especially, to effect the separation of manganese from other metals. 1, *a*, is generally preferred to 1, *b*, in cases where the choice is permitted. If the solution of manganese contains sugar or some similar non-volatile organic substance, neither 1, *a*, nor 1, *b*, is applicable, and recourse must be had to 1, *c*. The phosphate and borate of manganese are treated, either according to the directions of 1, *b*, as the salts precipitated from acid solution by potassa are completely decomposed upon boiling with excess of potassa, or according to the direction of 1, *c*. The proportion of manganese in the silicate of the protoxide is determined, after the separation of the silicic acid (§ 140), according to the directions of 1, *a*; for the analysis of chromate of protoxide of manganese, see § 130 (chromic acid). The estimation of manganese from the quantity of chlorine disengaged upon boiling the oxides of the metal with hydrochloric acid, is resorted to, more particularly, to determine the degrees of oxidation of manganese, and permits also the estimation of manganese in presence of other metals.

1. *Determination as Protosesquioxide of Manganese.*

a. By Precipitation as Carbonate of Protoxide of Manganese.

The precipitation and washing are effected in exactly the same way as directed § 108, *a* (determination of zinc as oxide, by precipitation as carbonate); the precipitate is dried, and then ignited as directed § 53. The lid is removed from the crucible, and the heat maintained at a high degree of intensity, until the weight of the residue remains constant. Care must be taken to prevent reducing gases finding their way into the crucible. For the properties of the precipitate and residue, see § 78. This method, if properly executed, gives accurate results. The principal point is to continue the application of a sufficiently intense heat long enough to effect the object in view. It is necessary also to ascertain whether the residue has not an alkaline reaction, and whether it dissolves in hydrochloric acid without leaving silica.

b. By Precipitation as Hydrated Protoxide of Manganese.

Precipitate the solution of the salt under examination in a platinum or silver dish, with solution of pure soda or potassa, and proceed in all other respects as in *a.*

If phosphoric acid is present, or boracic acid, the fluid must be kept boiling for some time with an excess of alkali. For the properties of the precipitate, see § 78. The method gives accurate results.

c. By Precipitation as Sulphide of Manganese.

Mix the manganese solution in a flask, with chloride of ammonium, then if the fluid is acid, with ammonia, until the reaction is neutral, or remains only very slightly acid; add yellow sulphide of ammonium in moderate excess; let the precipitate subside in a warm place; then decant the supernatant fluid through a filter; wash three times by decantation, and, at last, thoroughly, and without interruption, on the filter, with water mixed with a little yellow sulphide of ammonium. Put the moist filter with the precipitate into a beaker, pour dilute hydrochloric acid over it, and warm until the mixture smells no longer of sulphuretted hydrogen; filter, wash the residuary paper carefully, and proceed with the filtrate as directed in *a.*

d. By Separation as Binoxide of Manganese.

Heat the solution of the acetate of protoxide of manganese or some other compound of the protoxide containing but little free acid, after addition of a sufficient quantity of acetate of soda, to from 122° to 140° F., and transmit chlorine gas through the fluid. The whole of the manganese present falls down as binoxide (*Schiel,—Rivot, Beudant*, and *Daguin*). Wash, first by decantation, then upon the filter; dry, transfer the precipitate to a flask, add the filter ash, heat with hydrochloric acid, filter, and precipitate as directed in *a.* I cannot recommend the direct conversion of the precipitated binoxide into protosesquioxide by ignition, as that body has an extraordinary tendency to take up alkali. The separation of manganese as binoxide, by evaporating the solution of the manganese compound in nitric acid to dryness, and heating the residue, finally to 311° F., is given in the fifth section.

e. By direct Ignition.

The manganese compound under examination is introduced into a platinum crucible, which is kept closely covered at first, and exposed to a gentle heat; after a time the lid is taken off, and replaced loosely on the crucible, and the heat is increased to the highest degree of intensity, with careful exclusion of reducing gases; the process is continued until the weight of the residue remains constant. The conversion of the higher oxides of manganese into protosesquioxide of manganese requires a more intense heat (hardly attainable by any other means than by a gas blowpipe-lamp), and a more protracted application of it than the conversion of the protoxide and sesquioxide. In the case of salts of manganese with organic acids, care must always be taken to ascertain whether the whole of the carbon has been consumed; and should the contrary turn out to be the case, the residue must either be redissolved in hydrochloric acid, and the solution precipitated, &c., as directed in *a*, or it must be repeatedly evaporated with nitric acid, until the whole of the carbon is oxidized. The method, if properly executed, gives accurate results. In the ignition of salts of manganese with organic acids, minute particles of the salt are generally carried away with the empyreumatic products evolved in the process, which, of course, tends to reduce the weight.

2. *Determination as Sulphate of Protoxide of Manganese.*

The same method as in the case of magnesia under the same circumstances; see § 104, *b*, 1. Care must be taken, more particularly, to expose the residue to a faint red heat only, and to avoid too great an excess of sulphuric acid. For the properties of the residue, see § 78. The results are generally a little too low, as a minute quantity of sulphuric acid is apt to escape if the heat applied exceeds faint redness.

§ 110.

3. PROTOXIDE OF NICKEL.

a. Solution.

Many of the salts of protoxide of nickel are soluble in water. The pure protoxide, in its common modification, and those of its salts which are insoluble in water, dissolve, without exception, in hydrochloric acid. The peculiar modification of protoxide of nickel, discovered by *Genth*, which crystallizes in octahedra, does not dissolve in acids, but is rendered soluble by fusion with bisulphate of potassa. Metallic nickel dissolves slowly, with evolution of hydrogen gas, when warmed with dilute hydrochloric or sulphuric acid; in nitric acid, it dissolves with great readiness. Sulphide of nickel is but sparingly soluble in hydrochloric acid, but it dissolves readily in nitrohydrochloric acid. Peroxide of nickel dissolves in hydrochloric acid, upon the application of heat, to protochloride, the solution being attended with evolution of chlorine.

b. Determination.

Protoxide of nickel is always weighed as such (§ 79). The compounds of nickel are converted into the pure protoxide, either by precipitation as hydrated protoxide, preceded, in some instances, by precipitation as sulphide of nickel, or by ignition.

We may convert into

PROTOXIDE OF NICKEL.

a. By Precipitation as Hydrated Protoxide of Nickel.	*b. By Precipitation as Sulphide of Nickel.*
All the salts of nickel with inorganic acids which are soluble in water, and all its salts with volatile organic acids; likewise all salts of nickel which, insoluble in water, dissolve in the stronger acids, with separation of their acid.	All compounds of nickel without exception.

c. By Ignition.

The salts of nickel with organic acids, and with readily volatile oxygen acids, or with such oxygen acids as are decomposed at a high temperature (carbonic acid, nitric acid).

The method *c*, when it is applicable, is preferable to the other methods, more especially in the case of salts of nickel with the inorganic acids pointed out in *c*. The method *a* is most frequently resorted to. If sugar or some other non-volatile organic substance is present, this must either be destroyed by ignition before proceeding to the solution and precipitation of the compound under examination, or the method *b*, of which the application otherwise is almost exclusively confined to effect the separation of the protoxide of nickel from other bases, must be resorted to. The methods of estimating the protoxide of nickel in its combinations with chromic acid, phosphoric acid, boracic acid, and silicic acid, will be found in Part II. of this section, under the heads of the several acids.

Determination as Protoxide of Nickel.

a. By Precipitation as Hydrated Protoxide of Nickel.

Mix the solution with pure solution of potassa or soda in excess, heat for some time nearly to ebullition, decant 3 or 4 times, filter, wash the precipitate *thoroughly* with hot water, dry and ignite (§ 53). The best vessel to effect the precipitation in is a platinum dish; in presence of nitrohydrochloric acid, or, if the operator does not possess a sufficiently capacious dish of that metal, in a porcelain dish; glass vessels do not answer the purpose so well. Presence of ammoniacal salts, or of free ammonia, does not interfere with the precipitation. For the properties of the precipitate and residue, see § 79. This method, if properly executed, gives very accurate results. The thorough washing of the precipitate is a most essential point. It is necessary also to ascertain whether the residue has not an alkaline reaction, and whether it dissolves completely in hydrochloric acid.

b. By Precipitation as Sulphide of Nickel.

This requires the greatest care and attention. The best way is to proceed according to either of the two subjoined methods.

α. The moderately dilute solution of nickel is, if necessary, neutralized with ammonia (the reaction should be rather slightly acid than alkaline): colorless perfectly saturated hydrosulphate of sulphide of ammonium is then added as long as a precipitate continues to form, care being taken, however, not to add the reagent in too considerable excess. The mixture is now well stirred, passed on to a moistened filter, and the precipitate thoroughly washed by a continuous stream of distilled water, to which one or two drops of colorless perfectly saturated hydrosulphate of sulphide of ammonium have been added. The filtrate washings and the rinsing water must be perfectly colorless. The precipitate is then dried in the funnel, and subsequently removed as completely as possible from the filter, and transferred to a beaker; the filter is incinerated in a coil of platinum wire, or upon the lid of a crucible, and the ash added to the dry precipitate. The precipitate is now treated with concentrated nitrohydrochloric acid, and the mixture digested at a gentle heat, until the whole of the sulphide of nickel is dissolved, and the undissolved sulphur appears of a pure yellow; the fluid is then diluted, filtered, and the filtrate precipitated, &c., as directed in *a*. For the properties of the precipitate, see § 79. The method, if properly executed, gives accurate results.

If the solution contains ammonia, or if yellow sulphide of ammonium is used as precipitant, the fluid filtered off from the sulphide of nickel possesses always a more or less brownish tint, and contains sulphide of nickel, which it is found a difficult task to remove completely by exposure to air. If the filter were not incinerated, but treated at once, together with the precipitate, with nitrohydrochloric acid, the solution of the sulphide of nickel would contain an admixture of organic substances, and the soda or potassa would accordingly afterwards fail to effect the complete precipitation of the nickel.

β. Mix the slightly acidified solution of nickel with bicarbonate of ammonia, so as to retain the free acid present, and leave besides the disengaged carbonic acid, still a slight excess of bicarbonate of ammonia in the solution; transmit hydrosulphuric acid gas through the mixture. Precipitation will promptly ensue. Filter, and treat the precipitate as in *α*.

c. By direct Ignition.

The same method as described § 109, 1, *e.* (Manganese.)

§ 111.

4. PROTOXIDE OF COBALT.

a. Solution.

Protoxide of cobalt and its compounds behave with solvents like the corresponding compounds of nickel; metallic cobalt like metallic nickel. The protosesquioxide of cobalt which has recently been obtained by *Schwarzenberg* in microscopic octahedra does not dissolve in boiling hydrochloric acid, or nitric acid, nor in nitrohydrochloric acid; but it dissolves in concentrated sulphuric acid, and after fusing with bisulphate of potassa.

b. Determination.

The accurate estimation of cobalt presents considerable difficulties, since, as *Fremy* has shown, the hydrated protoxide thrown down by alkalies is not pure, as was formerly supposed, but invariably retains traces of the acid and a not inconsiderable admixture of the alkaline precipitant which washing fails to remove. I thought the metal reduced from the oxide by hydrogen gas might be freed from all extraneous matter by boiling with water; but I found that it could not be accomplished: the metallic powder, though repeatedly boiled with water, still continues to impart a brown tint to turmeric paper if left in contact with it for some time. The old method of estimating cobalt, by precipitating that metal with alkalies, in the form of hydrated protoxide, must, accordingly, be altogether discarded where accurate results are required.

The best forms into which to convert the protoxide of cobalt for quantitative estimation, are, *metallic cobalt*, *protosesquioxide of cobalt*, *sulphate of protoxide of cobalt*, and *nitrite of sesquioxide of cobalt and potassa.* The conversion of the protoxide into the sulphate is often preceded by precipitation as sulphide of cobalt.

We may convert into

1. METALLIC COBALT.

All salts of cobalt that may be reduced directly by hydrogen gas (sesquichloride of cobalt, nitrate of protoxide of cobalt, carbonate of protoxide of cobalt, &c.).

2. PROTOSESQUIOXIDE OF COBALT (Co_2O_3, $Co\,O$).

Sesquioxide of cobalt and nitrate of protoxide of cobalt.

3. SULPHATE OF PROTOXIDE OF COBALT.

All compounds of cobalt without exception.

4. NITRATE OF SESQUIOXIDE OF COBALT AND POTASSA.

All compounds of cobalt soluble in water or acetic acid.

1. *Determination as Metallic Cobalt.*

Evaporate the solution of sesquichloride of cobalt, or of nitrate of protoxide of cobalt, which must be free from sulphuric acid and alkali, in a weighed platinum crucible, to dryness; cover the crucible with a lid having a small aperture in the middle, conduct through this a moderate current of pure dry hydrogen gas, and then apply a gentle heat, which increase gradually to intense redness. When the reduction is considered complete, let the reduced metal cool in the current of hydrogen gas, and weigh; ignite again in the same way and repeat the process until the weight of the reduced metal remains constant. The results are accurate. For the properties of cobalt, see § 80.

Fig. 61 shows the arrangement of the reducing apparatus.

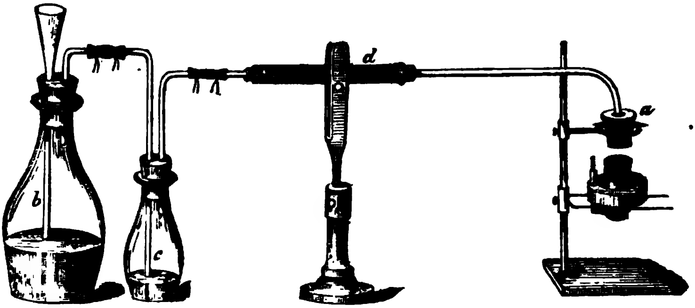

Fig. 61.

a is the crucible with the compound of cobalt, *b* the evolution flask; *c* contains sulphuric acid, *d* chloride of calcium.

2. *Determination as Protosesquioxide of Cobalt.*

Heat the nitrate of protoxide of cobalt, or the pure sesquioxide, to intense ignition, and repeat the process until the weight remains constant. For the properties of the residue, see § 80. The results are accurate.

3. *Determination as Sulphate of Protoxide of Cobalt.*

a. By direct Conversion.

The solution is evaporated to dryness, in a platinum dish or platinum crucible* — (directly, if it contains sulphate of protoxide of cobalt; but if it contains a volatile acid, after previous addition of a slight excess of sulphuric acid)—and the residue cautiously heated, at a gradually increased temperature, which is finally raised to gentle redness: the application of heat is continued until no more fumes escape and the weight of the crucible remains constant.

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* At least, towards the end of the process of evaporation.

After weighing, the salt is treated with hot water. If this fails to effect complete solution (a sign that the salt has become basic) the residue is dissolved in hydrochloric acid, and the amount of sulphuric acid is then estimated in the solution, as directed § 132; the quantity of the protoxide of cobalt being finally estimated from the difference. The results are accurate.

For the properties of sulphate of protoxide of cobalt, see § 80.

b. Preceded by Precipitation as Sulphide of Cobalt.

Mix the solution with a little chloride of ammonium, and add ammonia in very slight excess, then sulphide of ammonium until the formation of a precipitate ceases; let the precipitate subside, decant repeatedly, adding a few drops of sulphide of ammonium each time to the water; filter, wash with water mixed with a little sulphide of ammonium, dry, and redissolve as directed § 110, *b.* (Sulphide of nickel.)

The solution obtained contains invariably sulphuric acid; the amount of the cobalt is determined as directed in the preceding section (3. *a*) taking care to evaporate the fluid, which contains nitrohydrochloric acid, in a porcelain dish, with addition of sulphuric acid, to dryness, before transferring the residue, with a little water, to the platinum dish. The results are accurate.

For the properties of the sulphide of cobalt, see § 80.

4. *Determination as Nitrite of Sesquioxide of Cobalt and Potassa* (used principally in cases of separation).

Mix the cobalt solution, which must not be too dilute (at the most, 300 parts of water to 1 of protoxide of cobalt), with a concentrated solution of nitrite of potassa; add acetic acid in quantity a little more than sufficient to redissolve the precipitate, which is at first produced in the solution by the free potassa and carbonate of potassa contained in the nitrite of that alkali. Cover the beaker with a shallow glass dish, and let it stand 12 to 24 hours in a warm place. Filter the yellow precipitate on a weighed filter, wash thoroughly with an aqueous solution of neutral acetate of potassa (containing 10 per cent. of the salt), displace, finally, the last traces of solution of acetate of potassa still adhering to the precipitate, by means of spirit of wine of 80 per cent., dry at 212° F., and weigh. The method gives very satisfactory results (*A. Stromeyer*, "Annal. der Chem. u. Pharm.," 96, 218). For the properties of the precipitate, see § 80.

§ 112.

5. PROTOXIDE OF IRON.

a. Solution.

Many of the compounds of protoxide of iron are soluble in water. The compounds insoluble in water dissolve almost without exception in hydrochloric acid, in which the pure protoxide also is soluble; the solutions, if not prepared with perfect exclusion of air, and with solvents absolutely free from air, contain invariably more or less sesquichloride. In cases where it is wished to avoid the chance of peroxidation, the solution of the compound of protoxide of iron is effected in a small flask, through which a slow current of carbonic acid gas is transmitted, the transmission of the gas being continued until the solution is cold. Some native compounds of iron require fluxing with carbonate of soda, as an indispensable preliminary to their solution in hydrochloric acid. The solutions so prepared contain a large proportion of the iron as sesquichloride. Metallic iron dissolves in hydrochloric acid, and in dilute sulphuric acid, with evolution of hydrogen, as protochloride or sulphate of protoxide; in warm nitric acid it dissolves as nitrate of sesquioxide, and in nitrohydrochloric acid as sesquichloride.

b. Determination.

The amount of protoxide of iron in a compound may be determined either by converting the protoxide into sesquioxide, and weighing the latter, or by volumetrical analysis. Both methods are applicable in all cases. For the way of estimating the quantity of protoxide of iron by the amount of gold reduced by its agency from the terchloride of that metal, see supplement to § § 112 and 113.

1. *Determination as Sesquioxide of Iron.*

The solution of the protoxide is converted into solution of sesquioxide, and afterwards treated as directed, § 113. In some cases (see § 113), and especially in the separation of the protoxide of iron from other oxides, the protoxide is first precipitated as sulphide of iron in the manner described § 113.

The following is the best method of peroxidising a solution of protoxide of iron:—

Mix the solution of the protoxide of iron with a little hydrochloric acid, if it does not already contain that acid; add some nitric acid, and heat the mixture for some time to incipient ebullition. The color of the fluid will show whether the nitric acid has been added in sufficient quantity. Though an excess of nitric acid does no harm, still it is better to avoid adding too much on account of the subsequent precipitation. In concentrated solutions, the addition of nitric acid produces a dark-brown color, which disappears upon heating. This color is owing to the nitric oxide formed dissolving in the still undecomposed portion of the solution of the protoxide.

The conversion of the protoxide into sesquioxide may likewise be effected by transmitting chlorine gas through the solution, or by adding to it chlorine water in excess, or by heating the hydrochloric acid solution with chlorate of potassa.

2. *Estimation by Volumetric Analysis.*

a. Marguerite's Method.

This method is based upon the following principle:—

If we add to a solution of protoxide of iron, containing an excess of acid permanganate of potassa, the former is peroxidised, at the expense of the latter, which suffers reduction [$10\ \mathrm{Fe\,O, S\,O_3} + 8\ \mathrm{S\,O_3} + \mathrm{K\,O, Mn_2O_2} = 5\ (\mathrm{Fe_2O_3}, 3\ \mathrm{S\,O_3}) + \mathrm{K\,O, S\,O_3} + 2\ (\mathrm{Mn\,O, S\,O_3})$]. Now if we know how much iron will be converted from the state of protoxide to that of sesquioxide, by a given volume of a solution of permanganate of potassa, we can, by this means, readily determine an unknown quantity of iron; we need simply, for this purpose, dissolve the iron in a small quantity of concentrated hydrochloric, or, better, dilute sulphuric acid, in the form of protoxide, peroxidize the largely diluted solution accurately, and see how many volumes of the solution of permanganate of potassa have been used to accomplish that object.

a. Determination of the Strength ("Standard" or "titre") of the Solution of Permanganate of Potassa.

The process of preparing a standard solution of permanganate of potassa for volumetrical purposes having been described already in § 65, 3, I will at once proceed to give the several methods employed to determine the strength of the solution.

Either of the three subjoined methods may be selected for the purpose; or, the strength having been determined by one method, it may, by way of control, be determined once more by one of the other methods.

As solution of permanganate of potassa suffers gradual decomposition, though only to a trifling extent, each analysis, made after an interval of even only a day, must be preceded by a fresh determination of its strength.

aa. Determination of the Strength by means of Metallic Iron.

Weigh off accurately about 0·2 grm. of thin, clean iron wire (pianoforte wire), free from rust; introduce this into a small long-necked flask, add about 20 cubic centimetres of dilute sulphuric acid, and the same quantity of water, and close the flask with a cork, bearing a glass tube bent at a right angle. Secure the flask in an oblique position, by means of a retort-holder, so that the outer limb of the tube is turned downward; then heat the fluid to gentle ebullition. As soon as the iron is dissolved, remove the cork, fill the flask to two-thirds with distilled water, and place it in cold water until quite cold; smear the rim with a little tallow, then pour the contents cautiously into a beaker of about 400 cubic cent. capacity, and transfer the last particles from the flask to the beaker by repeated rinsing with cold water. The total quantity of fluid should be about 200 cub. cent. Place the beaker on a sheet of white paper.

Fill a *Gay-Lussac's* or *Geissler's* burette of 30 cub. cent. capacity, divided into $\frac{1}{10}$ cub. cent. (see § 22, Figs. 19 and 20), up to zero, with solution of permanganate of potassa, of which take care to have ready a sufficient quantity, perfectly and uniformly mixed.

Now add, from the burette, solution of permanganate of potassa to the iron solution, taking care to stir the latter all the while with a glass rod. At first the red drops disappear very rapidly, gradually more slowly. The fluid, which at first was nearly colorless, gradually acquires a yellowish tint. From the instant the red drops begin to disappear more slowly, use great caution in adding the solution of permanganate of potassa, restricting the quantity to single drops; keep on adding solution of permanganate of potassa, drop by drop, until the last drop imparts to the fluid a faint, but unmistakeable reddish color, which remains on stirring. A little practice will enable you readily to hit the right point constantly. As soon as the fluid in the burette has sufficiently collected again, read off, and mark the number of cub. cent. used. Be very careful in this operation (see § 22), to make no mistake, particularly as regards the correct number of the $\frac{1}{10}$ cubic cent. divisions.

If 0·2 grm. of iron have taken from 20 to 30 cub. cent. of solution of permanganate of potassa, the latter may be considered to be of the proper degree of concentration for most determinations of iron. If much less has been used in the process, the solution is too concentrated. In that case add to the entire quantity a sufficient amount of water to give it approximately the right degree of concentration; then repeat the above experiment with a fresh amount of iron. If, on the other hand, considerably more than 30 cub. cent. of solution of permanganate of potassa have been used in the process, the solution, though not exactly unfit for use, ought still to be rejected, and a stronger solution prepared; as the operation becomes more tedious and inconvenient in proportion as the degree of concentration falls below the above standard.

When you have completed the experiment with a solution of approximately proper concentration, calculate, by a simple proportion, how much iron 100 cubic centimetres of the solution will convert from the state of protoxide to that of sesquioxide. Supposing, for instance, you have used to 0·210 grm. of iron, 23·5 cubic cent. of the solution of permanganate of potassa, then

$$23{\cdot}5 \text{ c.c.} : \text{o. } 210 \text{ grm.} :: 100 \text{ c.c.} : x \text{ grm. } x = 0{\cdot}8936 \text{ grm.}$$

As the accuracy of all valuations made with the solution of permanganate of potassa depends upon the correct determination of the strength, it is always advisable to repeat the experiment.

As even the purest iron wire is not chemically pure, but contains a little carbon, it is always advisable in analyses requiring the very highest degree of accuracy, to reduce the weight of the iron wire used in the process, by multiplication with 0·997, to the corresponding weight of chemically pure iron. This reduction is based upon the generally correct supposition that the wire contains 0·3 per cent. of extraneous matter.

If, in the two experiments made for the purpose of determining the strength of the solution of permanganate of potassa, the quantities of iron respectively corresponding to 100 cubic centimetres of solution, differ only about 1, 2, or 3 milligrammes per gramme, the results may be considered perfectly satisfactory. But if the difference is considerably greater, a third experiment must be made.

Instead of dilute sulphuric acid, dilute hydrochloric acid may be employed to effect the solution of the iron; but in that case, the greater care is required not to use the iron solution in too concentrated a state, or whilst still warm; otherwise chlorine will be evolved, and the experiment will give less accurate results. If there is a deficiency of free acid in the solution of iron, the fluid acquires a brown color, turns turbid, and deposits a brown precipitate (binoxide of manganese + sesquioxide of iron). The same may happen also if the solution of permanganate of potassa is added too quickly, or if the proper stirring of the iron solution is omitted or interrupted. Experiments attended with abnormal manifestations of the kind had always better be rejected. That the fluid reddened by the last drop of solution of permanganate of potassa added, loses its color again after a time, need create no surprise or uneasiness; this decolorisation is, in fact, quite inevitable, as a dilute solution of permanganate of potassa cannot keep long undecomposed.

bb. Determination of the Strength by means of Sulphate of Protoxide of Iron and Ammonia.

Weigh off, with the greatest accuracy, about 1·4 grm. of the pure salt prepared according to the directions given in § 65, 4, after powdering the crystals, and pressing gently between sheets of smooth blotting-paper. Dissolve in about 200 cubic centimetres of distilled water, add about 20 cubic centimetres of dilute sulphuric acid, and proceed as in *aa.*

As sulphate of protoxide of iron and ammonia contains exactly $\frac{1}{7}$th of its weight of iron, the calculation required to show the value of 100 cubic centimetres of solution of permanganate of potassa is very simple. Supposing, for instance, 25 cubic centimetres of the solution of permanganate of potassa to have been consumed to 1·400 grm. of the salt of iron, then,

$$\frac{1{\cdot}4}{7} = 0{\cdot}2$$

$$25 : 0{\cdot}2 :: 100 : x ; \; x = 0{\cdot}8$$

If the sulphate of protoxide of iron and ammonia used is not pure, if, for instance, it contains bases isomorphous with protoxide of iron (protoxide of manganese, magnesia, &c.); or if it contains sesquioxide, or is used in a moist condition, the result will necessarily give a slightly greater strength for the permanganate of potassa solution; since, under the circumstances mentioned, the quantity of protoxide of iron, and accordingly of iron, contained in the amount of salt in reference to which the determination of the standard solution of permanganate of potassa has been made, is assumed at a higher figure than is really present.

cc. Determination of the Strength by means of Oxalic Acid.

This method is based upon the following principle:—

If solution of permanganate of potassa is added to a warm solution of oxalic acid, mixed with sulphuric acid, the liberated permanganic acid instantly oxidizes the oxalic acid to carbonic acid ($5\,C_2O_3 + 3\,S_3O + KO, Mn_2O_7 = 10\,CO_2 + 2\,MnO, SO_3 + KO, SO_3$). The oxidation of 1 equivalent of oxalic acid and 2 equivalents of iron (in the state of protoxide) requires, accordingly, equal quantities of permanganic acid; therefore, 63 parts (1 equivalent) of crystallized oxalic acid corresponds, in reference to the oxidizing action of permanganic acid, to 56 parts (2 equivalents) of iron.

By dissolving 63 grammes of pure crystallized oxalic acid (§ 65, 1) in water to 1 litre of fluid, a so-called normal, or standard solution, of oxalic acid is obtained, which finds frequent application in acidimetry and alkalimetry. By diluting 100 cubic centimetres of this standard solution with water to 1 litre of fluid, a standard solution ten times more dilute is produced, which is quite suited to the purpose here in view. 50 cubic centimetres of this solution, which correspond to 0·315 grammes of crystallized oxalic acid, or 0·28 grammes of iron, are introduced into a flask, diluted with about 100 cubic centimetres of water, from 6 to 8 cubic centimetres of concentrated sulphuric acid added, and the fluid heated to about 140° F. The flask is then placed on a sheet of white paper, and solution of permanganate of potassa added from the burette, with agitation of the flask. If the process is properly conducted throughout, the red drops disappear at first very rapidly, after some time instantaneously, without the least smell of chlorine* becoming perceptible. As soon as the red drops begin to disappear more slowly, the solution of permanganate of potassa must be added with great caution; if proper care is taken in this respect, it is easy to complete the reaction with a single drop of solution of permanganate of potassa; this completion of the reaction is indicated with beautiful distinctness in the colorless fluid. The number of cubic centimetres used corresponds to 0·28 grammes of iron.

If the oxalic acid is not perfectly dry, or not quite pure, the result of the experiment will, of course, lead to fixing the strength of the solution of permanganate of potassa too high.

Of the foregoing three methods of determining the standard solution of permanganate of potassa, the first is the one originally proposed by *Marguerite*. Sulphate of protoxide of iron and ammonia was first proposed by *Fr. Mohr*, oxalic acid by *Hempel*, as agents suitable for the purpose. With absolutely pure and thoroughly dry reagents, and proper attention, all those methods give correct and corresponding results.

I prefer the first of the three methods, as the most direct and positive, the only doubtful point about it being the question whether the assumption that the iron wire contains 99·7 per cent. of chemically pure iron is quite correct; this, however, is of very trifling importance, as the extremest limit of a presumable error in this assumption could not possibly exceed $\frac{1}{10}$ or, at the most, $\frac{1}{20}$ per cent. But the other two methods are, as may readily be seen, somewhat more convenient, since in one of them the trouble is saved of preparing the solution of iron, &c., and in the other there is, moreover, no need of weighing.

For the analysis of very dilute solutions of iron, *e.g.* ferruginous mineral waters, in which the amount of iron may be very approximately determined with great expedition, by direct oxidation with solution of permanganate of potassa, a very dilute standard solution must be prepared; of which 100 cubic centimetres correspond to 0·1 grm. of iron.

In experiments of the kind, the fact that a certain quantity of solution of permanganate of potassa is required to impart a distinct color to pure acidified water (which is of no consequence in operations where the concentrated solution is used) must be taken into consideration; for where the solution used is so highly dilute, it takes indeed a measurable quantity of it to impart the desired reddish tint to the amount of water employed.

In the case of very dilute solutions of iron, therefore, it is necessary either to employ for the determination of the standard solution of permanganate of potassa, a solution of iron, or of sulphate of protoxide of iron and ammonia, made with boiled water free from air, and containing about the same proportion of iron as the mineral water, &c., to be examined is supposed to contain, and to use equal volumes for the determination of the standard and the examination of the ferruginous fluid; or to determine by special experiments how many $\frac{1}{10}$ cubic centimetres of the standard solution of permanganate of potassa are required to impart the desired reddish tint to a volume of pure acidified water, equal to that of the iron solution employed to determine the standard, and the solution of protoxide under examination. By deducting the number of $\frac{1}{10}$ cubic centimetres so found from that of the volumes of solution of permanganate of potassa used in determining the standard and examining the ferruginous fluid, we find the correct number of volumes actually consumed to effect the peroxidation of the protoxide of iron.

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* Solution of permanganate of potassa contains much chloride of potassium.

β. Performance of the Analytical Process.

This has been fully indicated in *α*. The compound to be examined is dissolved, if necessary, with application of a current of carbonic acid (§ 112 *a*.), in water, dilute sulphuric acid, or hydrochloric acid, and the solution suitably diluted (if practicable, the solution of a substance containing about 0·2 grm. of iron should be diluted to about 200 cubic centimetres); if free acid is not yet present in sufficient quantity, about 20 cub. cent. of dilute sulphuric acid are added, and then standard solution of permanganate of potassa from the burette, to incipient reddening of the fluid. The volume of standard solution used is then read off. The standard of the solution of permanganate of potassa being known, the quantity of iron present in the examined fluid is found by a very simple calculation. Supposing 100 cub. cent. of solution of permanganate of potassa to correspond to 0·98 grm. of iron, and 25 cub. cent. of the solution to have been used to effect the peroxidation of the protoxide of iron in the examined compound, then

$$100 : 0{\cdot}98 :: 25 : x;\ x = 0{\cdot}245.$$

The quantity of iron originally present in the form of protoxide amounted accordingly to 0·245 grm.

For the method of determining the total amount of iron present in a solution containing both protoxide and sesquioxide of that metal, I refer to § 113; for that of determining the respective separate amounts of the sesquioxide and of the protoxide, to Section V.

b. Penny's method (recommended subsequently by *Schabus*).

If bichromate of potassa is added to a strongly acid solution of protoxide of iron, the latter is converted into sesquioxide, whilst the chromic acid is reduced to sesquioxide of chromium ($6\,FeO + 2\,CrO_3 = 3\,Fe_2O_3 + Cr_2O_3$).

Now, with 0·1 eq. of bichromate of potassa = 14·867 grm. dissolved to 1 litre of fluid, 0·6 eq. = 16·8 grm. of iron may be converted from the state of protoxide to that of sesquioxide, and 50 cub. cent. of the above solution correspond accordingly to 0·84 grm. of iron.

Care must be taken to use perfectly pure bichromate of potassa; the salt is heated in a porcelain crucible until it is just fused; it is then allowed to cool under the desiccator, and the required quantity weighed off when cold. Besides the ordinary standard fluid, another should also be prepared, ten times more dilute, and containing accordingly 0·01 eq. of bichromate of potassa in the litre.

It is always advisable to test the correctness of the standard of the solution of bichromate of potassa, by peroxidizing with it a known amount of pure iron dissolved to protoxide (see § 112, 2, *a*, *α*, *aa*).

The analytical process is performed as follows:—

The solution of protoxide of iron is sufficiently diluted, mixed with a sufficient quantity of hydrochloric or dilute sulphuric acid, and the standard solution of bichromate of potassa slowly added from the burette, the liquid being stirred all the while with a thin glass rod. The fluid, which is at first nearly colorless, speedily acquires a pale green tint, which changes gradually to a darker chrome-green. A very small drop of the mixture is now from time to time taken out by means of the stirring-rod, and brought into contact with a drop of a solution of ferricyanide of potassium on a porcelain plate, on which a great many drops of that solution are sprinkled for the purpose. When the blue color thereby produced begins to lose the intensity which it exhibited on the first trials, and to assume a paler tint, the addition of the solution of bichromate of potassa must be more carefully regulated than at first, and towards the end of the process, a fresh essay must be made, and with larger drops than at first, after each new addition of two drops, and finally, even of a single drop; drops must also be left for some time in contact before the observation is taken. When no further blue coloration ensues, the oxidation is terminated. From the remarkable sensitiveness of the reaction, the exact point may be easily hit to a drop. To heighten the accuracy of the results, the dilute (ten times weaker) standard fluid should, towards the end of the process, be substituted for the concentrated solution of bichromate of potassa.

If exactly 0·84 grm. of the substance to be analysed have been dissolved, the number of half cub. cent. used of the concentrated standard fluid shows how many per cents. that of the half cub. cent. used of the dilute standard fluid, how many tenths per cent. of pure iron the analysed substance, contains in the form of protoxide. For the manner of proceeding in presence of sesquioxide of iron, I refer to § 113. If there is a deficiency of free acid in the solution, brown chromate of sesquioxide of chromium may form, upon which the solution of protoxide of iron exercises no longer a deoxidizing action.

Of the two preceding volumetrical methods, the first has the advantage that the termination of the process of oxidation is clearly indicated by the reddening of the solution; whilst the second, on the other hand, has this very essential point in its favor—that the solution of bichromate of potassa may be easily prepared, and kept unaltered.

§ 113.

6. Sesquioxide of Iron.

a. Solution.

Many of the compounds of sesquioxide of iron are insoluble in water. Pure sesquioxide of iron and most of those of its compounds which are insoluble in water, dissolve in hydrochloric acid, but many of them only slowly and with difficulty; compounds of this nature are best dissolved in concentrated hydrochloric acid, in a flask, with the aid of heat; which, however, should not be allowed to reach the boiling point; the compound must, moreover, be finely comminuted, and even then it will often take many hours to effect complete solution. Iron ores insoluble in hydrochloric acid are rendered soluble by ignition with carbonate of soda.

b. Determination.

Sesquioxide of iron is invariably weighed as such (§ 81). It may, however, be estimated also indirectly, and also by volumetrical analysis, after previous reduction to protoxide. The conversion of compounds of iron into sesquioxide is effected either by precipitation as hydrated sesquioxide, preceded in some cases by precipitation as sulphide of iron, or as succinate or basic acetate of sesquioxide of iron; or by ignition.

We may convert into

SESQUIOXIDE OF IRON.

a. By Precipitation as Hydrated Sesquioxide.

All soluble salts of iron with inorganic or volatile organic acids, and likewise those which, insoluble in water, dissolve in hydrochloric acid, with separation of their acid.

b. By Precipitation as Sulphide of Iron.

All compounds of iron without exception.

c. By Precipitation as Succinate of Sesquioxide of Iron ; and

d. By Precipitation as Basic Acetate of Sesquioxide of Iron.

The compounds enumerated sub. *a.*

e. By Ignition.

All salts of sesquioxide of iron with volatile oxygen acids.

The method *e* is most expeditious and accurate, and is therefore preferred in all cases where its application is admissible. The method *b* serves principally to effect the separation of the sesquioxide of iron from other bases; it is resorted to also in certain instances where *a* is inapplicable, especially in cases where sugar or other non-volatile organic substances are present; and also to estimate the sesquioxide of iron in its compounds with phosphoric acid and boracic acid. The methods *c* and *d* are used exclusively to effect the separation of the sesquioxide of iron from other bases. For the manner of determining the sesquioxide of iron in the chromate and silicate, I refer to § 130 and § 140.

1. *Determination as Sesquioxide of Iron.*

a. By Precipitation as Hydrated Sesquioxide of Iron.

Mix the solution in a dish or beaker with ammonia in excess, heat nearly to boiling, decant repeatedly on to a filter, wash the precipitate *carefully* with hot water, dry *thoroughly* (which very greatly reduces the bulk of the precipitate), and ignite in the manner directed in § 53.

For the properties of the precipitate and residue, see § 81. The method is free from sources of error. The precipitate must, under all circumstances, even in the absence of fixed bodies requiring removal by washing, be most *carefully* and *thoroughly* washed, since, should it retain any traces of chloride of ammonium, a portion of the iron would volatilize in the form of sesquichloride. It is also highly advisable to dissolve the weighed residue, or a portion of it, in strong hydrochloric acid, to see whether the sesquioxide is quite free from silicic acid.

b. By Precipitation as Sulphide of Iron.

The iron compound under examination is dissolved in its appropriate menstruum, in a flask or beaker, and ammonia added to complete neutralization of the free acid present. (In the absence of organic non-volatile substances this leads to the precipitation of a little hydrated sesquioxide of iron, which, however, is of no consequence.) Yellowish sulphide of ammonium is then added in excess, the mixture well stirred, and a gentle heat applied. The operator generally obtains in this manner a black precipitate in a colorless or yellowish fluid, in which case he may at once proceed to filtration; but should the fluid exhibit a greenish color—which happens particularly with very dilute solutions, and is owing to extremely minute particles of sulphide of iron remaining mechanically suspended in the fluid—the flask, closed with a cork, or the beaker covered with a glass plate, must be kept at rest in a moderately warm place, until the geenish tint has changed to yellow, when the fluid may be filtered. In either case, the filtration and washing must proceed without interruption; the water used for washing the precipitate is mixed with a small quantity of sulphide of ammonium; the funnel is kept well covered during the operation. Neglect of any of these precautions will occasion some loss of substance, the sulphide of iron gradually combining with the oxygen of the air, and passing thus into the filtrate as sulphate of protoxide of iron. As this sulphate is reprecipitated by the sulphide of ammonium present, the filtrate assumes, in such cases, a greenish color, and gradually deposits a black precipitate. If the quantity of the precipitate is rather considerable, it is highly advisable to wash in the first place repeatedly by decantation, before transferring the precipitate to the filter; the water used for the purpose must also contain sulphide of ammonium. The fluids are not decanted on to a filter, but poured into a flask, and then, when the washing by decantation is completed, the entire fluid decanted is passed through the filter before the precipitate is transferred to it.

When the operation of washing is completed, the moist precipitate is put, together with the filter, into a beaker, some water added, and then hydrochloric acid, until the whole of the sulphide of iron present is redissolved. Heat is now applied, until the solution smells no longer of sulphuretted hydrogen; the fluid is then filtered into a flask, the filter carefully washed, and the filtrate peroxidized by heating with nitric acid (see § 112, 1); the peroxidized solution is finally precipitated with ammonia, as in *a.*

If a solution of potassio-, sodio-, or ammonio-tartrate of sesquioxide of iron contains a considerable excess of alkaline carbonate, the precipitation of the iron as sulphide is prevented to a greater or less extent (*Blumenau*). In such cases the fluid must therefore be nearly neutralized with an acid, before the precipitation with the sulphide of ammonium can be effected.

c. By Precipitation as Succinate of Sesquioxide of Iron.

The salt of iron under examination is dissolved in the appropriate menstruum, in a flask, and very dilute solution of ammonia added, drop by drop, until a small portion of the iron precipitates in the form of hydrated sesquioxide; a gentle heat is then applied, to ascertain whether or not the precipitate will redissolve. If it redissolves, the addition of dilute ammonia is continued, until the application of heat fails to redissolve the precipitate formed. If, on the contrary, it remains undissolved, and the fluid continues to exhibit a brownish red color, all the preliminary conditions requisite for precipitation with succinate of ammonia are fulfilled. But should the fluid appear colorless, this is a sign that too much ammonia has been added; in which case it will be necessary to add a small portion of hydrochloric acid, and then again some ammonia until the desired point is attained. To the fluid thus prepared is now added a perfectly neutral solution of succinate of ammonia, as long as a precipitate forms; a gentle heat is then applied, and the fluid allowed to cool; when perfectly cold, it is filtered, and the precipitate washed, first with cold water, finally with warm solution of ammonia — which operation, depriving the precipitate in a very great measure of its acid, imparts a darker tint to it. The washed precipitate is dried upon the filter in the funnel, and then converted into sesquioxide of iron, by ignition (§ 53). The object of washing the precipitate with ammonia is to remove part of the acid, since, were this neglected, and the precipitate simply washed with water, a portion of the sesquioxide of iron might suffer reduction upon the subsequent ignition of the succinate. If there is reason to apprehend that this has actually taken place, some nitric acid is poured over the precipitate, evaporated, and the ignition repeated. For the properties of the precipitates, see § 81. The results are accurate.

d. By Precipitation as Basic Acetate of Sesquioxide of Iron.

Mix the solution of sesquioxide of iron, in a flask, if it contains much free acid, with carbonate of soda or ammonia until the acid is nearly neutralized; then add to the still clear, but already somewhat darker colored solution, neutral acetate of soda or neutral acetate of ammonia in slight excess; and heat nearly to boiling; continue this application of heat until the precipitate formed has clearly subsided. Wash repeatedly by boiling and decantation, and finally on the filter with boiling water; dry, ignite (§ 53), and weigh the sesquioxide obtained. It is advisable to add a few drops of nitric acid to the residue, evaporate and ignite again, to see whether the weight remains constant. The residue must show no alkaline reaction when moistened with water. The results are accurate.

e. By Ignition.

Expose the compound, in a covered crucible, to a gentle heat at first, which increase gradually to the highest degree of intensity; continue the operation until the weight of the residuary sesquioxide of iron remains constant.

2. *Determination by Volumetrical Analysis.*

The volumetrical methods here given are based upon the reduction of the sesquioxide to protoxide, and estimation of the quantity of the latter. We have, accordingly, to occupy ourselves here simply with the reduction of the solution of the sesquioxide, the other part of the process having been fully discussed in § 112 (Protoxide of Iron).

a. Reduction by Zinc.

Heat the hydrochloric acid or sulphuric acid solution, which must contain an excess of acid, but be as free as possible from nitric acid, in a small long-necked flask, placed in a slanting position; drop in small pieces of metallic zinc, perfectly free from iron (§ 60), and close the flask with a perforated cork, into which is fitted a tube, bent at a right angle. Evolution of hydrogen gas begins at once, and the color of the solution becomes paler in proportion as the sesquioxide changes to protoxide. Apply a moderate heat, to promote the operation; and add also, if necessary, a little more zinc. As soon as the solution is completely decolorized, and all the zinc dissolved, dip the point of the bent tube in water, and remove the lamp from under the flask, by which means some water will recede and enter the flask; repeat the same operation until the flask is two-thirds full; then let it completely cool, and proceed as directed in § 112, 2, *a*, *β*. If the solution contains metals pecipitable by zinc, these will separate, and render filtration necessary. As long as there remains any undissolved zinc in the iron solution, the volumetrical analysis cannot properly be proceeded with; if, therefore, too much of that metal has been added, the fluid must also first be filtered before proceeding with the determination of the amount of iron in it. In cases where zinc free from iron cannot be procured, the quantity of iron contained in the metal must be determined, and weighed portions of it employed in the process of reduction; the known amount of iron contained in the quantity of zinc consumed in the operation is then subtracted from the total amount of iron found.

b. Reduction by Sulphuretted Hydrogen.

Mix the warm hydrochloric acid solution, in a flask, with saturated sulphuretted hydrogen water in excess; or, if you have larger quantities of substance to deal with, conduct sulphuretted hydrogen gas into it, until the fluid smells strongly of that gas; place the flask in a slanting position, heat to gentle ebullition, and continue this until the sulphuretted hydrogen is completely expelled. There is no necessity to filter off the precipitated sulphur.

c. Reduction by Sulphite of Soda.

Mix the hydrochloric acid solution, in a flask, with a concentrated solution of soda, and boil. If the first portion of sulphite of soda added, prove insufficient to reduce the whole of the sesquioxide of iron, a fresh portion must be added. The boiling must be continued until the disengagement of sulphurous acid has entirely ceased.

Of these three methods of reduction *a* is certainly by far the best; *b* and *c* are liable to lead to mistakes, more particularly the latter, as it is difficult to free a fluid completely from sulphuretted hydrogen, and still more to free it from sulphurous acid, without the risk of causing reoxidation of the protoxide of iron.

Supplement to §§ 112 *and* 113.

Besides the methods given in §§ 112 and 113, there are several others by which the quantitative estimation of iron may be effected; some of these are old methods, others have been proposed lately. However, as they either are by no means superior to those described in detail in the foregoing §§ (112 and 113), or find only limited application, I confine myself here to a mere brief description of the most important among them.

a. Indirect Gravimetrical Methods.

1. *Fuch's* method ("Journ. f. prakt. Chem.," 17, 160). The solution, which contains the iron as sesquioxide, and must be free from nitric acid, is mixed with hydrochloric acid, and boiled with weighed strips of metallic copper, until the fluid has become light green; the quantity of iron is estimated from the loss of weight of the copper ($Fe_2\,Cl_3 + 2\,Cu = 2\,Fe\,Cl + Cu_2\,Cl$). The method gives neither very accurate nor very constant results (*J. Löwe*, "Journ. f. prakt. Chem.," 61, 127; *J. R. Brant*, "Chem. Centralbl.," 1854, 864; *E. Ebermayer*, "Journ. f. prakt. Chem.," 70, 143).

2. The solution, which contains the iron as sesquioxide, and must be free from metals of the fifth and sixth groups, as well as from other substances exercising a decomposing action upon sulphuretted hydrogen, is precipitated with clear sulphuretted hydrogen water in excess, all application of heat being avoided. After a few days the precipitated sulphur is collected, &c., and weighed; the amount of sesquioxide of iron is estimated from the weight found after the formula ($Fe_2\,O_3 + HS$

$= 2\,FeO + HO + S$). (*H. Rose.*) Results accurate. Compare *Delff's* "Chem. Centralbl.," 1856, 839.

3. The solution, which contains the iron as protoxide, is mixed with sodio-terchloride of gold in excess, the flask closed, and the reduced gold which separates determined. $6\,Fe\,Cl + Au\,Cl_3 = 3\,Fe_2\,Cl_3 + Au$. (*H. Rose.*) Results accurate.

4. The solution, which contains the iron as protoxide, is mixed with a slight excess of bichromate of potassa; the excess of the bichromate is estimated from the amount of carbonic acid which is disengaged by treating with oxalic acid (§ 130), and the quantity of the iron calculated from the amount of bichromate of potassa required to effect its peroxidation. (*Vohl*, "Annal. d. Chem. u. Pharm.," 94, 218). The method is complicated and difficult to execute with accuracy, as it is necessary to employ a strongly concentrated solution of the protoxide of iron.

b. Volumetrical Methods.

1. The solution, which contains the iron as sesquioxide, is mixed with a not inconsiderable excess of iodide of potassium, solution of protochloride of tin, of which the standard has been determined by bichromate of potassa, added until the brown color has become light; starch-paste is then added, and finally again solution of protochloride of tin, until the iodide of starch is just decomposed. (*Duflos*, "Journ. f. prakt. Chem.," 65, 184.) The method deserves little commendation. (Compare *Casselmann*, "Annal. d. Chem. u. Pharm." 96, 129. *Kessler*, "Poggend. Annal.," 96, 332.)

2. The hydrochloric acid solution, which contains the iron as sesquioxide, is mixed with protochloride of tin, and warmed until it is colorless; the excess of the protochloride of tin is removed by chloride of mercury, and the protoxide of iron remaining unaltered, determined by means of a solution of bichromate of potassa. (*Kessler*, "Poggend. Annal.," 95, 204.) I do not think this method of reducing sesquioxide of iron to protoxide any way preferable to the reduction by zinc.

§ 114.

Supplement to the Fourth Group.

7. SESQUIOXIDE OF URANIUM.

If the compound in which the sesquioxide of uranium is to be determined contains no other fixed substances, the sesquioxide may often be converted into PROTOSESQUIOXIDE ($U\,O, U_2\,O_3$) by simple ignition. If sulphuric acid is present, small portions of carbonate of ammonia must be thrown into the crucible towards the end of the operation.

In cases where the application of this method is inadmissible, the solution of uranium (which, if it contains protoxide, must first be warmed with nitric acid, until the protoxide is converted into sesquioxide) is precipitated with ammonia. The yellow precipitate formed, which consists of hydrated AMMONIO-SESQUIOXIDE OF URANIUM, is washed with a dilute solution of chloride of ammonium, to prevent the fluid passing through the filter in a milky condition. The precipitate is dried and ignited (§ 53). To make quite sure to obtain the protosesquioxide in the pure state, the crucible is ignited for some time in a slanting position and uncovered; the lid is then put on, the process of ignition still continuing. The crucible is allowed to cool under the desiccator, and, when quite cold, weighed (*H. Rose*).

If the solution from which the sesquioxide of uranium is to be precipitated contains other bases (alkaline earths, or alkalies), portions of these, even the latter, will precipitate along with the sesquioxide of uranium. For the measures to be resorted to in such cases, I refer to Section V.

The reduction of the protosesquioxide of uranium to the state of protoxide (U O) is an excellent means of ascertaining its purity, by way of control. This reduction is effected by ignition in a current of hydrogen gas, in the way described § 111, 1 (cobalt). By intense ignition, the property of the protoxide of uranium to ignite in the air is destroyed. The separation of sesquioxide of uranium from phosphoric acid is effected by fusing the compound with cyanide of potassium and carbonate of soda. Upon lixiviating the fused mass, the phosphoric acid is obtained in solution, whilst the uranium is left as protoxide. *Knop* and *Arendt** have employed this method.

The equivalent of protosesquioxide of uranium is = 210·2, viz. 178·2 of uranium and 32 of oxygen. In 100 parts, the compound consists of 84·77 of uranium and 15·23 of oxygen. The equivalent of protoxide of uranium is 67·4, viz., 59·4 of uranium and 8 of oxygen; in 100 parts, the protoxide consists of 88·13 of uranium and 11·87 of oxygen.

FIFTH GROUP.

OXIDE OF SILVER—OXIDE OF LEAD—SUBOXIDE OF MERCURY—OXIDE OF MERCURY—OXIDE OF COPPER—TEROXIDE OF BISMUTH—OXIDE OF CADMIUM—(PROTOXIDE OF PALLADIUM).

§ 115.

1. Oxide of Silver.

a. Solution.

Metallic silver, and those of its compounds which are insoluble in water, are best dissolved in nitric acid (if soluble in that acid). Dilute nitric acid suffices for most compounds; sulphide of silver, however, requires concentrated acid. The solution is effected best in a flask. Chloride, bromide, and iodide of silver are insoluble in water and in nitric acid. To get the silver contained in them in solution, it must first be reduced to the metallic state, which may be readily effected in the following way:—fuse the salt in a porcelain crucible (this operation, though not absolutely indispensable, had better not be omitted), pour water over it, put a piece of clean zinc or iron upon it, and add some sulphuric or hydrochloric acid. Wash the reduced spongy silver, first with dilute sulphuric acid, then with water, and finally dissolve it in nitric acid. However, as we shall see below, the quantitative analysis of the chloride, bromide, and iodide of silver does not necessarily require the solution of these salts.

b. Determination.

Silver may be weighed as *chloride of silver*, *sulphide of silver*, *cyanide of silver*, or in the *metallic* state. It is also frequently determined by volumetrical analysis.

We may convert into

1. Chloride of Silver. 2. Sulphide of Silver. 3. Cyanide of Silver.

All compounds of silver without exception.

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* "Chem. Centralblatt," 1856, page 773.

4. Metallic Silver.

Oxide of silver, and some of its compounds with readily volatile acids; salts of silver with organic acids; chloride of silver.

The method 4 is the most convenient, and is preferred to the others in all cases where its application is admissible. The method 1 is that most generally resorted to. 2 and 3 serve mostly only to effect the separation of oxide of silver from other bases. In the assays of the Mint, the silver is usually determined by volumetrical analysis.

1. *Determination of Silver as Chloride.*

a. In the Humid Way.

The precipitated chloride of silver may be separated from the supernatant fluid either by decantation or by filtration; the former is generally preferred for large quantities of precipitate, the latter answers better for small quantities.

α. Determination by Decantation.

The moderately dilute solution of the compound under examination is introduced into a tall flask with long neck and narrow mouth, and some nitric acid added to it; the fluid is heated to about 140° F., and hydrochloric acid added as long as a precipitate forms. The mouth of the flask is then closed with a perfectly smooth cork (or, better still, with a well-ground glass stopper), and the flask vigorously shaken until the precipitated chloride of silver has united into coherent lumps, and the supernatant fluid has become pretty clear. The minute particles of chloride of silver which may still adhere to the sides of the neck of the flask are then rinsed down by means of a washing-bottle, and the stopper is loosely replaced. The flask is now put in a moderately warm place, until the precipitate has *completely* subsided, and the supernatant fluid has become *perfectly* clear and transparent, which generally requires several hours. The clear fluid is then slowly and cautiously decanted, as far as practicable, into a beaker, so as to retain every particle of the chloride in the flask, whence it is carefully transferred to an upright smooth porcelain crucible: the last particles of chloride of silver which remain adhering to the bottom and sides of the flask are rinsed into the neck of the latter with a little water—by inverting the flask, and closing its mouth with the finger—and likewise transferred to the crucible, by holding the mouth of the flask close over the latter, and letting the fluid run out; a washing bottle with the jet turned upwards (§ 46) may also be used with advantage.

When the chloride of silver has completely subsided in the crucible, which is greatly accelerated by exposure to the heat of a water-bath, the clear supernatant fluid is carefully decanted down a glass rod into the same beaker which contains the liquid of the first decantation. The chloride of silver in the crucible is moistened with a few drops of nitric acid, and then treated with hot distilled water; the chloride is again allowed to subside, the clear supernatant fluid again decanted, and the same operation repeated until a drop of the last decanted fluid occasions no longer the slightest turbidity in a solution of nitrate of silver. The last portions of supernatant fluid are then carefully and cautiously decanted, or removed by means of a pipette; the chloride is thoroughly dried on the water-bath, and subsequently heated to incipient fusion over the lamp, taking care to apply a very gentle heat at first; as soon as the chloride begins to fuse round the border, the crucible is removed from the flame, allowed to cool, and weighed.

To remove the mass from the crucible, completely and without injury to the latter, a piece of iron or zinc is placed upon the chloride, and highly dilute hydrochloric or sulphuric acid poured over it. The crucible is finally cleansed, dried, and weighed, if this has not been done before the operation. Should the liquids successively decanted from the chloride of silver not be perfectly clear and transparent, they are kept standing in a warm place until the last particles of chloride have completely subsided, which frequently requires many hours; the clear supernatant fluid is then decanted, and the deposited chloride added to the bulk of the precipitate in the crucible; or — and this is a more expeditious way—the minute quantity of chloride is collected on a small filter, treated as directed in β, and added to the principal amount.

β. Determination by Filtration.

The chloride of silver is precipitated and allowed to subside as in *a*; the supernatant fluid is then passed through a small filter, to which the precipitate is subsequently transferred, with the aid of a little hot water acidulated with nitric acid; the precipitate collected on the filter is washed, first with water acidulated with nitric acid, afterwards with pure water; it is then thoroughly dried, ignited (§ 53), and weighed. If the rules here laid down are strictly adhered to, there is no difficulty in the process of filtration. Care must be taken to remove the chloride as completely as possible from the filter before proceeding to incineration.

For the properties of the precipitate, see § 82. Both methods give very accurate results, though a trifling loss is incurred in β, owing to part of the minute portion of chloride of silver which, notwithstanding the greatest care, will always adhere to the filter, suffering reduction upon ignition, from the action of the carbonic oxide evolved by the combustion of the filter. This may be remedied, however, by putting the ash of the filter into the crucible, along with the chloride, adding a little dilute nitric acid, warming for some time, adding a few drops of hydrochloric acid, evaporating, drying, and igniting, as directed in *a*. Some chemists reckon the silver contained in the filter-ash at once as metallic silver.

b. In the Dry Way.

This method serves more exclusively for the analysis of bromide and iodide of silver, although it is adapted also for the quantitative estimation of other salts of silver.

The process is conducted in the apparatus illustrated by Fig. 62.

a is an apparatus for disengaging chlorine; *b* contains concentrated sulphuric acid, *c* chloride of calcium; *d* is intended for the reception of the iodide or bromide of silver; and *e* serves to conduct the chlorine gas into the open air or into milk of lime. The operation is commenced by introducing the compound to be analysed into the bulb *d*, and applying heat to the latter until its contents are fused; when cold, the tube is weighed and connected with the apparatus. Chlorine gas is then evolved from *a*; when the evolution of the gas has proceeded for some time, the contents of *d* are heated to fusion, and kept in this state for about fifteen minutes, agitating now and then the fused mass. The tube *d* is then removed from the apparatus, allowed to cool, and held in a slanting position to replace the chlorine by atmospheric air; it is subsequently weighed, then again connected with the apparatus, and the former process repeated, keeping the contents of *d* in a state of fusion for a few minutes. The operation may be considered concluded if the weight of the tube suffers no variation by the repetition of the process. This method, if properly executed, gives exceedingly accurate results.

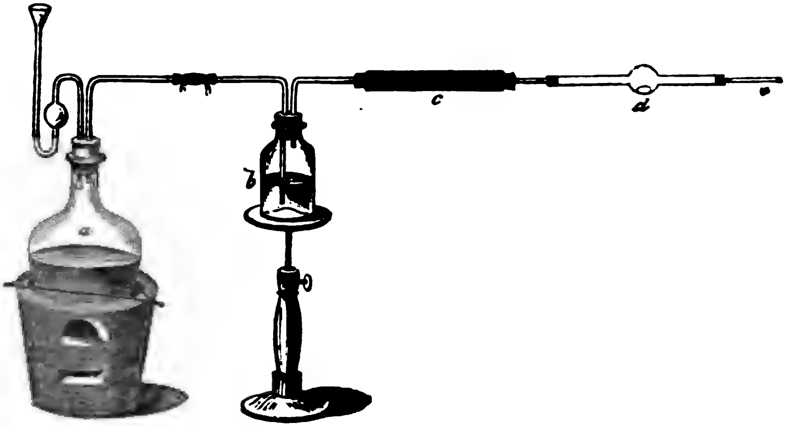

Fig. 62.

2. *Determination as Sulphide of Silver.*

Sulphuretted hydrogen precipitates silver completely from acid, neutral, and alkaline solutions; sulphide of ammonium precipitates it from neutral and alkaline solutions. Recently prepared perfectly clear solution of sulphuretted hydrogen may be employed to precipitate small portions of silver; to precipitate larger quantities, the solution of the salt of silver (which must not be too acid) is moderately diluted, and washed sulphuretted hydrogen gas conducted into it. The precipitated fluid is then gently heated, the sulphide of silver collected on a weighed filter, washed, dried at 212° F., and weighed. For the properties of the precipitate, see § 82. This method, if properly executed, gives very accurate results. The operator must take care to filter quickly, and to prevent the access of air as much as possible during the filtration, since, if this precaution be neglected, sulphur is likely to separate from the sulphuretted hydrogen-water, which, of course, would increase the apparent weight of the sulphide of silver.

If there is reason to suspect that sulphur has separated along with the sulphide of silver—owing either to imperfect exclusion of the air during filtration, or to the presence of sesquioxide of iron or some other substance likely to decompose sulphuretted hydrogen—the precipitate, together with the filter, must be digested, at a gentle heat, with moderately dilute nitric acid perfectly free from chlorine, until complete decomposition is effected, and the undissolved sulphur appears of a pure yellow; the solution is then filtered off from the sulphur, the latter carefully washed, and the filtrate and rinsing water treated as directed in 1. The separation of free sulphur along with the sulphide of silver may often be prevented, by adding to the silver solution cyanide of potassium until the precipitate which forms at first is redissolved, and precipitating the silver or sulphide from the solution so obtained.

3. *Determination as Cyanide of Silver.*

Mix the neutral or acid solution of silver with cyanide of potassium, until the precipitate which forms at first is redissolved; add nitric acid in slight excess, and apply a gentle heat. After some time, collect the precipitated cyanide of silver on a weighed filter, wash, dry at 212° F., and weigh. For the properties of the precipitate, see § 82. The results are accurate.

4. *Determination as Metallic Silver.*

Oxide of silver, carbonate of silver, &c., are easily reduced by simple ignition in a porcelain crucible. In the reduction of salts of silver with organic acids, the crucible is kept covered at first, and a moderate heat applied; after a time the lid is removed, and the heat increased, until the whole of the carbon is consumed. For the properties of the residue, see § 82. The results are absolutely accurate, except as regards salts of silver with organic acids; in the analysis of the latter, it not unfrequently happens that the reduced silver contains a minute portion of carbon, which increases the apparent weight of the silver; the difference, however, is only very trifling.

Chloride of silver is put into the bulb of a bulb-tube, fused and weighed. The tube is then connected with an apparatus for the evolution of dry hydrogen gas. (See Fig. 63.)

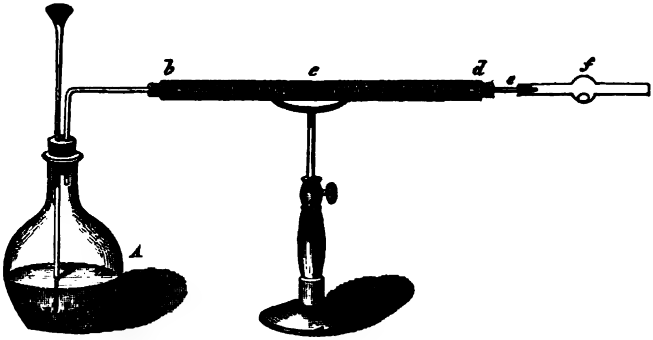

Fig. 63.

A is the evolution flask, containing granulated zinc; *b d*, a long glass tube, filled up to *c* with blotting-paper, and from *c* to *d* with chloride of calcium.

When the apparatus is completely filled with hydrogen, and the evolution of the gas proceeds steadily and slowly, the chloride of silver in the bulb is heated to fusion, and maintained at a moderate red heat, until no more fumes of chloride of ammonium are produced upon holding a glass rod moistened with ammonia to the aperture through which the gas escapes. The apparatus is then allowed to cool, the bulb-tube detached from it, and held some time in a slanting position, that the hydrogen still remaining in it may be replaced by atmospheric air; it is then finally weighed. The results are most accurate.

5. Determination by Volumetrical Analysis.

The determination of silver by volumetrical analysis is based upon the circumstance, that one equivalent of chloride of sodium throws down one equivalent of silver from solutions of that metal. We need therefore simply prepare a solution of chloride of sodium of known strength, and ascertain how much of this is required to throw down the whole of the silver from a solution of the metal. This method, which *Gay-Lussac* substituted for the assay of silver by cupellation, may be found described at length in *Gay-Lussac's* "Instructions on the Method of Assaying Silver in the Humid Way," translated into German by *J. Liebig*, published by *Vieweg*, of Brunswick. I shall here only give so much of the process as is required for use in the laboratory.

a. Preparation of the standard Solution of Chloride of Sodium.

One grm. of pure silver combines with 0·32844 grm. of chlorine, to form chloride of silver. This quantity of chlorine is contained in 0·54142 grm. of chloride of sodium. If, therefore, we dissolve 5·4142 grms. of chemically pure chloride of sodium in water, and add water to the solution until we have exactly one litre of fluid, measured at 59° F., 100 cubic centimetres of this fluid will correspond exactly to 1 grm., and 1 cubic centimetre accordingly to 0·01 grm. of silver. Besides this solution, one is required ten times more dilute, which is prepared by mixing 1 volume of the solution with 9 volumes of water. Each cubic centimetre of this dilute solution corresponds accordingly to 0·001 grm. of silver.

b. Preparation of the standard Solution of Silver, which is also required in this Volumetrical Method.

One grm. of chemically pure silver is dissolved in pure nitric acid, and the solution diluted to exactly one litre of fluid. Each cubic centimetre of this solution corresponds to 0·001 grm. of silver, which is precipitated exactly by 1 cubic centimetre of the dilute (decimal) solution of chloride of sodium.

c. Testing the standard Solutions.

One grm. of chemically pure silver is dissolved in 6 cubic centimetres of pure nitric acid, at a gentle heat; the solution is effected in a white flask with well-fitting glass stopper. The nitrous acid fumes are blown out of the flask, with the aid of a bent glass tube. Exactly 100 cubic centimetres of the concentrated solution of chloride of sodium at 59° F., are then added, the moistened glass stopper is inserted, and the mixture shaken until the chloride of silver formed has concreted into a lump, and the fluid become clear. One cubic centimetre of the dilute (decimal) solution of chloride of sodium is now added; if the solution has been correctly prepared, this must cause no turbidity. One cubic centimetre of the solution of silver is now added, and the fluid again shaken until it has recovered its clearness; another cubic centimetre of the solution of silver is then added, which again must cause no turbidity in the solution.

d. Performance of the Analytical Process.

It is, in the first place, necessary that the operator should have some *approximate* notion of the quantity of silver contained in the compound under examination (as is the case, for instance, in the assaying of coins, &c.). If not, he must have recourse to a preliminary assay; for this purpose, a portion of the substance under examination is weighed off, dissolved, if necessary, in nitric acid, and the concentrated solution of chloride of sodium added, drop by drop, from a burette; the mixture is shaken, and the addition of solution of chloride of sodium continued until no further precipitation takes place.

The quantity of silver in the salt or alloy having been thus approximately ascertained, a portion of it is weighed off, calculated to contain about 1 grm. of silver,* and, if a solid salt or alloy, dissolved in pure nitric acid in the flask mentioned in *c.* The nitrous acid fumes are blown out of the flask, and exactly 100 cubic centimetres of the concentrated solution of chloride of sodium of 59° F., are added by means of a pipette; the moistened glass stopper is then firmly inserted, and the mixture vigorously shaken until the chloride of silver has concreted into a lump, and the fluid become clear. It remains now to be ascertained whether the fluid still contains silver or chloride of sodium. To this end, 1 cubic centimetre of the dilute (decimal) solution of chloride of sodium is added to it; if the fluid turns turbid, this is a sign that the weighed quantity of the salt or alloy contained more than 1 grm. of silver. In that case, the fluid is shaken until the newly formed chloride has subsided, another cubic centimetre of the dilute solution of chloride of sodium is then added, and the same operation repeated, until the cubic centimetre last added leaves the fluid clear. It is generally assumed that only one half of the cubic centimetre added before the last was required, and 1·5 c. c. is accordingly subtracted from the amount of dilute solution of chloride of sodium used. The remaining number of cubic centimetres used gives the number of milligrammes of silver which the analysed sample contains over and above 1 grm.

If the first cubic centimetre added of the dilute standard solution of chloride of sodium leaves the fluid clear, 1 cubic centimetre of the standard silver solution is added, to throw down this chloride of sodium; the fluid is then shaken until the chloride of silver formed has subsided, and the fluid become clear again. Another cubic centimetre of the standard solution of silver is now added in the same way, and the same operation repeated until the cubic centimetre last added leaves the fluid clear. From the number of cubic centimetres used of the standard solution of silver, we have to subtract 2·5, viz., the first and the last added, and the one half of the one added before the last. The remaining number gives the number of milligrammes of silver which the analysed sample contains less than 1 grm.

For alloys containing sulphur, or consisting of gold and silver, and containing some tin, *Levol* ("Annal. de Chim. et de Phys.," 3 sér. 44, 347; "Journ. f. prakt. Chem.," 66, 382), employed concentrated sulphuric acid (about 25 grammes)—to effect the solution of the assay samples; the sample is boiled with the acid until dissolved; the fluid, after being allowed to cool a little, is treated in the ordinary way. However, as concentrated sulphuric acid, in presence of a large proportion of copper, fails to effect complete solution of the silver, *Mascazzini* ("Chem. Contralbl.," 1857, page 300) recommends first to digest the sample—which may, besides gold, contain also minute quantities of lead, tin, and antimony—with the least possible amount of nitric acid, as long as red fumes are evolved; then to add concentrated sulphuric acid, boil until the gold has completely subsided, let the mixture cool, add water, and then proceed with the analytical process.

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* In the case of coins, accordingly, which consist of 9 parts of silver and 1 of copper, about 1·115 to 1·120 grm. For this purpose the coin is screwed firmly in a vice, and a piece sawn out of it in a manner to make the two sides form radii of the circle. If the piece is too heavy for the purpose, the excess of weight is filed off.

Fr. Mohr has endeavoured to improve *Gay-Lussac's* method of determining silver. The following is the process which he recommends:—

Dissolve the sample presumed to contain silver and copper, in nitric acid, in a flask, and add concentrated standard solution of chloride of sodium to decided predominance, best to a divisional line marking ten volumes. Heat the contents of the flask to boiling, add crystallized carbonate of soda in moderate excess, boil until the oxide of copper has turned black, transfer the fluid, together with the precipitate, to a cylinder or flask of 150 cubic cent. capacity, rinse the flask with water, which transfer also to the measuring flask or cylinder, until the fluid, when quite cold, reaches exactly to 0; cover with a greased plate of vulcanized india-rubber, and shake. Let the solid particles now subside, take 50 cub. cent. of the clear fluid, add 2 or 3 drops of solution of neutral chromate of potassa, and determine the quantity of chloride of sodium in the fluid, as directed § 141. Multiply the resulting number by 3, and deduct the quantity of chloride of sodium so found from that first added; the difference expresses the quantity equivalent to the silver contained in the analysed compound.

This method, which is not likely, however, to supersede *Gay-Lussac's* at the Mint, may be useful in cases where the quantity of silver present is not approximately known. If you wish to employ it, make use of equivalent solutions: viz., a decimal solution of chloride of sodium, and a decimal solution of silver. To prepare the former, dissolve 5·846 grm. (0·1 eq.) of pure fused chloride of sodium to 1 litre of fluid; to prepare the latter, dissolve 10·797 grm. (0·1 eq.) of pure metallic silver, to 1 litre of fluid. There must be no excess of acid in the latter solution, which must consequently be treated as directed § 141.

The calculation in this method is not absolutely correct, as the precipitates of chloride of silver and oxide of copper are in the fluid when the latter is diluted to 150 cub. centimetres, and the 50 cub. centimetres taken out do not accordingly represent an absolute third of the solution; but the error is very trifling indeed, and disappears altogether if only a slight excess of solution of chloride of sodium has been added at first.

§ 116.

2. Oxide of Lead.

a. Solution.

Few of the salts of lead are soluble in water. Metallic lead, oxide of lead, and most of the insoluble salts of lead, dissolve in *dilute* nitric acid. Concentrated nitric acid effects neither complete decomposition nor complete solution, since, owing to the insolubility of nitrate of lead in concentrated nitric acid, the first portions of nitrate formed protect the yet undecomposed parts of the salt from the action of the acid. For the solubility of chloride and sulphate of lead, see § 83. As we shall see below, the analysis of these compounds may be effected without dissolving them. Iodide of lead does not dissolve in cold dilute nitric acid; but upon application of heat it dissolves readily with separation of iodine. Solution of potassa is the only menstruum in which chromate of lead dissolves without decomposition; for the purpose of analysis, the chromate is best converted into the chloride (see below). Sulphide of lead is usually converted at once into sulphate (see § 116, 6, β).

b. Determination.

Lead may be weighed as *oxide, sulphate, chromate, sulphide, chloride,* or as *oxide of lead + lead;* it may be determined also by volumetrical analysis.

We may convert into

1. Oxide of Lead.

a. By Precipitation.

All salts of lead soluble in water, and those of its salts which, insoluble in that menstruum, dissolve in nitric acid, with separation of their acid.

b. By Ignition.

α. Salts of oxide of lead with readily volatile or decomposable inorganic acids.

β. Salts of lead with organic acids.

2. Sulphate of Lead.

a. By Precipitation.

Those of the insoluble salts of lead of which the acid cannot be removed from solution in nitric acid.

b. By Evaporation.

α. All the oxides of lead, and also the salts of oxide of lead with volatile acids.

β. Many of the organic compounds of lead.

3. Chromate of Lead.

The compounds of lead soluble in water or in nitric acid.

4. Chloride of Lead.

Chromate, iodide, and bromide of lead.

5. Oxide of Lead + Lead.

Many of the organic compounds of lead.

6. Sulphide of Lead.

All salts of lead in solution. This method serves to separate lead from other substances.

The application of these several methods must not be understood to be rigorously confined to the compounds specially enumerated under their respective heads; on the contrary, all the compounds enumerated sub 1, may likewise be determined as sulphate of lead; and all those enumerated sub 1, 2, and 5, as sulphide of lead, &c. &c. Chloride, bromide, and iodide of lead are most conveniently reduced to the metallic state in a current of hydrogen gas, in the manner described § 115, 4 (reduction of chloride of silver), if not deemed preferable to dissolve them in water, or to decompose them by a boiling solution of carbonate of soda. If the reduction method is resorted to, the heat applied should not be too intense, since this might cause some chloride of lead to volatilize.

The higher oxides of lead are reduced by ignition to the state of simple oxide, and may thus be readily dissolved and analysed. Should the operator wish to avoid having recourse to ignition, the most simple mode of dissolving the higher oxides of lead is to act upon them with dilute nitric acid, with the addition of alcohol. For the methods of analysing sulphate, chromate, iodide, and bromide of lead, I refer to the paragraphs treating of the corresponding acids, in the second part of this section.

To effect the quantitative estimation of lead in the oxide and in many salts of lead, especially also in the sulphate, the compound under examination may be fused with cyanide of potassium, and the metallic lead obtained well washed, dried, and weighed. From the sulphide also the greater portion of the lead may be separated by this method, but never the entire (*H. Rose*, "Poggend. Annal.," 91, 104).

1. *Determination of Lead as Oxide.*

a. By Precipitation.

α. By Precipitation as Carbonate of Lead.

Mix the moderately dilute solution of the compound to be analysed with carbonate of ammonia slightly in excess, add some caustic ammonia, apply a gentle heat, and, after some time, filter. Wash the precipitate with pure water, dry, and ignite in a porcelain crucible, having previously incinerated the filter on the lid. For the properties of the precipitate and residue, see § 83. The results are satisfactory, although generally a trifle too low, owing to carbonate of lead not being absolutely insoluble, particularly in fluids rich in ammoniacal salts (Experiment No. 44). A small and thin filter should be used, and care taken to remove the precipitate as completely as practicable before proceeding to incineration; otherwise additional loss of substance might be incurred, from reduction of the adhering particles of the carbonate to metallic lead, by the carbon of the filter.

β. By Precipitation as Oxalate of Lead.

The solution of the compound under examination is mixed with oxalate of ammonia in excess, and ammonia added until it slightly predominates; the precipitated oxalate is then allowed to subside, the fluid filtered off, and the further process conducted as directed in *α*; the porcelain crucible is left uncovered during the ignition of the precipitate. Results as in *α*.

b. By Ignition.

Compounds like carbonate or nitrate of lead are cautiously ignited in a porcelain crucible, until the weight remains constant. For the manner of reducing salts of lead with organic acids to the state of oxide, see 5.

2. *Determination as Sulphate of Lead.*

a. By Precipitation.

α. Mix the solution (which should not be over dilute) with moderately dilute pure sulphuric acid slightly in excess, and add to the mixture double its volume of spirit of wine; wait a few hours, to allow the precipitate to subside; filter, wash the precipitate with spirit of wine, dry, and ignite, after the method described in § 53. Though a careful operator may use a platinum crucible, still a thin porcelain crucible is preferable. A small and thin filter should be employed, and the adhering sulphate of lead carefully removed before proceeding to incineration (see 1, *a*, *α*).

β. In cases where the addition of spirit of wine is inadmissible, a greater excess of sulphuric acid must be used, and the precipitate, which is allowed some time to subside, filtered, and washed first with water acidulated with a few drops of sulphuric acid, then repeatedly with spirit of wine. The remainder of the process is conducted as in *α*.

For the properties of the precipitate, see § 83. The method α gives very accurate results; those obtained by β are nearly equally accurate, provided the proper excess of sulphuric acid be used, and the washing water properly acidulated with that acid. Neglect of the former condition will, in the presence, for instance, of ammoniacal salts, nitric acid, &c., cause a portion of the lead to remain in solution; neglect of the latter will lead to the solution of perceptible traces of the precipitate in the washing water.

b. By Evaporation.

Put the weighed substance into a weighed dish, dissolve in dilute nitric acid, add moderately dilute pure sulphuric acid slightly in excess, and evaporate, at a gentle heat, at last high over the lamp, until the excess of sulphuric acid is completely expelled. In the absence of organic substances, the evaporation may be effected in a platinum dish; but if organic substances are present, a light porcelain dish is preferable. With due care in the process of evaporation, the results are perfectly accurate.

β. Organic compounds of lead are converted into the sulphate by treating them, in a porcelain crucible, with pure concentrated sulphuric acid in excess, evaporating cautiously in the well-covered crucible, until the excess of sulphuric acid is completely expelled, and igniting the residue. Should the latter not look perfectly white, it must be moistened once more with sulphuric acid, and the operation repeated. The method gives accurate results; a trifling loss is, however, usually incurred, the escaping sulphurous and carbonic acid gas being liable to carry away traces of the salt.

3. *Determination as Chromate of Lead.*

Mix the neutral or slightly acid solution with neutral chromate of potassa in excess, and, if free nitric acid has been present, add acetate of soda in sufficient quantity to replace the free nitric acid by free acetic acid; let the precipitate subside, at a gentle heat, and pass the fluid through a weighed filter dried at 212° F.; wash the precipitate with water, dry at 212° F., and weigh. For the properties of the precipitate, see § 93. The results are accurate.

4. *Determination as Chloride of Lead.*

Mix the solution with hydrochloric acid in excess, concentrate in the water-bath, treat the residue with absolute alcohol, mixed with ether, let the precipitate subside, filter off the fluid, wash the precipitate with alcohol mixed with ether, dry, and expose to a gentle heat; were you to heat it to redness, some of the chloride of lead would volatilize. In other respects the operation is conducted as directed in 1, *a*, α. This method is had recourse to in certain separations of lead from other substances.

5. *Determination as Oxide of Lead + Lead.*

Heat from one to two grms. of the organic compound of lead in a small weighed porcelain dish very gently, taking care to make the heat act first upon the rim of the dish, so that the ensuing decomposition may begin on one side, and proceed slowly. When the whole mass is perfectly decomposed, increase the heat a little, and continue until no more glowing particles are perceptible, and the residue forms a mixture of oxide of lead with globules of metallic lead, *perfectly* free from carbon. Weigh the residue; then heat it with acetic acid until the oxide is completely dissolved, which does not take long; pour off the solution now from the metallic lead, and wash the latter by repeated decantation; remove the last traces of water by heat, and weigh the residuary metallic lead. By subtracting the weight of the metal from that of the original residue, you will find the quantity of oxide of lead which was present in that residue; and by calculating the proportion of metal contained in the oxide, and adding the resulting number to the weight of the metallic lead, you will obtain the total amount of that metal originally present in the analysed compound. This method is very convenient, and, if properly and carefully executed, gives very accurate results. The operator must take care to conduct the decomposition of the organic compound very slowly, since the *rapid* combustion of its carbon and hydrogen, at the expense of the oxygen of the oxide of lead, would produce so high a temperature as to volatilize a portion of the lead in visible fumes. If the residue is not perfectly free from carbon —which will always be detected in the heating of it with acetic acid— this will tend to give a higher number.

This method was originally introduced by *Berzelius*. *Dulk* has recommended the following modification:—The compound to be analysed is gently heated, in a covered porcelain crucible, until the organic substance is completely carbonized; the lid is then removed, and the mass stirred with a piece of iron wire. Upon this, the mass begins to ignite, and a mixture of oxide of lead with metallic lead results, which may still contain unconsumed carbon. A few crystals of recently fused nitrate of ammonia are now thrown into the crucible, which has previously been removed from the flame, and the lid is again put on. The salt fuses, oxidizes the lead, and converts it partly into nitrate. The crucible is now exposed to a red heat, until no more fumes of hyponitric acid escape. The residuary oxide is then weighed. This modification of *Berzelius'* method gives very accurate results. It possesses this great advantage, that it ensures the complete combustion of the whole of the carbon; it saves also some trouble in weighing and calculating.

6. *Determination as Sulphide of Lead.*

a. The same method which serves for the determination of silver as sulphide (§ 115, 2,) may also be resorted to for lead; with this exception, however, that the precipitation of the sulphide of lead from acid solutions must be effected without the application of heat; otherwise, a portion of the precipitate will redissolve. The operator should also, before proceeding to filtration, test a portion of this supernatant fluid with a comparatively large quantity of saturated sulphuretted hydrogen water, to see whether it will remain clear. This experiment is intended to guard against errors arising from incomplete precipitation of the lead, by hydrosulphuric acid, from acid solutions. Compare *M. Martin*, "Chem. Centralbl.," 1856, 501. For properties of the precipitate, see § 83.

β. If the precipitate contains sulphur, it must be converted into sulphate of lead. To that end, it is dried on the filter, and put into a beaker, into which the filter is then also thrown; pure fuming nitric acid is now added, drop by drop, the beaker being kept covered with a glass plate. When the oxidation is effected, a gentle heat is applied for some time, and the contents of the beaker are then transferred to a small porcelain dish, the last particles being carefully rinsed into the latter; a few drops of pure sulphuric acid are now added, the mixture is cautiously evaporated, and the residue finally ignited. The results are accurate. The use of the *fuming* nitric acid is indispensable, the application of an acid of a lower degree of concentration involving always a separation of sulphur, which oxidizes in the subsequent process only with extreme slowness.

7. *Determination of Lead by Volumetrical Analysis.*

Although there is no lack of proposed methods of effecting the quantitative estimation of lead in the volumetrical way, not one of the processes recommended can be said to be really good; that is to say, applicable in all, or, at least, in most cases, and at the same time simple and accurate. As the gravimetrical method of estimating lead is, therefore, sure to be preferred for the present, to the volumetrical processes, a brief enumeration of the latter will suffice here.

a. The lead is precipitated as oxalate of lead, as directed in 1, *a*, β; the well washed precipitate is dissolved in nitric acid, sulphuric acid added, and the oxalic acid in the solution determined by permanganate of potassa (§ 137) *Hempel.* This method may be modified as follows: add to the solution of lead, in a measuring flask of 300 cub. cent. capacity, a measured quantity of oxalic acid in slight excess, then ammonia to slight predominance, fill the flask up to the mark, shake, let deposit, take out 100 cub. cent. of the clear fluid, determine the oxalic acid in it by permanganate of potassa (§ 137), multiply the quantity found by 3, deduct the product from the amount of oxalic acid contained in the solution first added, and reckon for every equivalent of oxalic acid, 1 equivalent of lead (*Fr. Mohr*, "Lehrbuch der Titrirmethode, page 198). This method gives accurate results, but requires very great care.

b. The chromic acid in the chromate of lead produced by precipitation, and thoroughly washed, is determined volumetrically, and 1 equivalent of lead reckoned for every equivalent of acid found. For this purpose, chromate of lead is treated with hydrochloric acid and a measured quantity of a solution of protochloride of iron of known strength. Sesquichloride of iron, sesquichloride of chromium, and chloride of lead are formed. The excess of protochloride of iron is determined in the fluid filtered from the chloride of lead, and the quantity of iron peroxidized calculated from this. Every 3 equivalents of peroxidized iron correspond to 1 equivalent of lead (*H. Schwarz*, "Annal. d. Chem. u. Pharm." 84, 92). The results are pretty accurate, but the process is rather complicated.

c. The methods proposed by *Flores Domonte* (precipitation of an alkaline solution of lead, with a standard solution of sulphide of sodium), and by *Marguerite* (precipitation of lead as binoxide, from a strongly alkaline solution by a standard solution of permanganate of potassa), are inconvenient and inaccurate.

§ 117.

3. SUBOXIDE OF MERCURY.

a. Solution.

Suboxide of mercury and its compounds may generally be dissolved by means of dilute nitric acid, but without application of heat if conversion of any of the suboxide into oxide is to be avoided. If all that is required, is to dissolve the mercury, the easiest way is to warm the substance for some time with nitric acid, then add hydrochloric acid, drop by drop, and continue the application of heat until a perfectly clear solution is produced, which now contains all the mercury as oxide and chloride.

b. Determination.

If it is impracticable to produce a solution of the suboxide, or its compounds, perfectly free from oxide, and where it becomes accordingly necessary to convert the mercury completely into oxide, the latter is determined as directed (§ 118). But if a solution of suboxide has been obtained, quite free from oxide, the quantitative determination of the suboxide may be based upon the insolubility of subchloride of mercury, and effected either gravimetrically or volumetrically. The process of determining mercury, described § 118, 1, *a*, may, of course, be applied equally well in the case of compounds of suboxide of mercury.

1. *Determination as Subchloride of Mercury.*

Mix the cold highly dilute solution with solution of chloride of sodium, as long as a precipitate forms; let the precipitate subside, filter on a weighed filter, dry at 212°F., and weigh. For the properties of the precipitate, see § 84. Results very accurate.

2. *Volumetrical Method.*

Mix the cold solution with decimal standard solution of chloride of sodium (§ 115, *5*, *d*), until this no longer produces a precipitate, and is accordingly present in excess; filter and wash thoroughly, taking care, however, to limit the quantity of water used; add a few drops of solution of chromate of potassa, then pure carbonate of soda, sufficient to impart a light yellow tint to the fluid, and determine by means of solution of nitrate of silver (§ 141), the quantity of chloride of sodium in solution, consequently the quantity which has been added in excess; this shows, of course, also the amount of chloride of sodium consumed in effecting the precipitation. One equivalent of Hg_2O is reckoned for every equivalent of Na Cl, consequently for every cub. cent. of the decimal solution of chloride of sodium, 0·02081 grm. of suboxide of mercury in solution. As filtering and washing form indispensable parts of the process, this method affords no great advantage over the gravimetrical; however, the results are accurate (*Fr. Mohr*, "Lehrbuch der Titrirmethode," 2, 62). The two methods, 1 and 2, may also be advantageously combined.

§ 118.

4. OXIDE OF MERCURY.

a. Solution.

Oxide of mercury, and those of its compounds which are insoluble in water, are dissolved, according to circumstances, in hydrochloric acid or in nitric acid. Sulphide of mercury is heated with hydrochloric acid, and nitric added until complete solution ensues. When a solution of chloride of mercury is evaporated on the water-bath, chloride of mercury escapes with the aqueous vapor. This circumstance must not be lost sight of in effecting the solution of compounds of mercury. It is from this cause that the method proposed by *Vohl* ("Annal. d. Chem. u. Pharm.," 94, 220), gives quite inaccurate results.

b. Determination.

Mercury may be weighed in the *metallic* state, or as *subchloride* or *sulphide*, or as *oxide*. In some cases the mercury is expelled from the analysed compound by ignition, and its amount inferred from the diminution of weight which the ignited compound has suffered. Mercury may be determined also by volumetrical analysis.

The methods of determining mercury as metal, subchloride, or sulphide, are applicable in all cases without exception; the latter, however, deserves the preference in most instances, on account of its accuracy, simplicity, and facility. The method of determining mercury as oxide can be resorted to only in the case of compounds of suboxide or oxide of mercury with nitric acid. The volumetrical method can be resorted to only occasionally, as the several conditions required for its application are rarely found united.

1. *Determination as Metallic Mercury.*

a. In the Dry Way.

The process is conducted in the apparatus illustrated by Fig. 64.

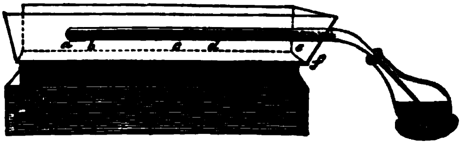

Fig. 64.

The principal part of the apparatus consists of a tube one and a half foot long, and between three and four lines wide, made of difficultly fusible glass, and sealed at one end. Into this tube is put, in the first place, a layer of dry hydrate of lime, which is passed down to the closed end, where it occupies a space of two inches in length, from *a* to *b*. This is followed by an intimate mixture of the mercurial compound, with an excess of soda-lime (§ 66, 5), which occupies the space from *b* to *c*. The particles of the mixture adhering to the mortar are removed with the aid of some more soda-lime, which is then also put into the tube, where it occupies the space from *c* to *d*. This is followed by a layer of pure soda-lime, occupying the space from *d* to *e*, and this again by a loose stopper of pure asbestos, from *e* to *f*. The anterior end of the tube is then drawn out, and bent at a somewhat obtuse angle. The manipulations in the processes of mixing and filling being the same as in ultimate or elementary analysis of organic bodies, they will be found described in detail in the chapter on that subject.

A few gentle taps upon the table is sufficient to shake the contents of the tube down so as to leave a free passage through the whole length of the tube. The tube, so prepared and arranged, is now placed in a combustion furnace, the point being inserted into a receiving flask containing water, of which it must just touch the surface sufficiently to have the opening half closed.

The tube is now surrounded with red-hot charcoal, in the same way as in organic analysis, proceeding slowly from *e* to *a*, the last traces of mercurial vapor being expelled by heating the hydrate of lime in the sealed end of the tube. Whilst the tube still remains in a state of intense ignition, the neck is cut off at *f*, and carefully and completely rinsed into the receiving flask, by means of a washing-bottle. The small globules of mercury which have distilled over are united into a large one, by agitating the flask, and, after the lapse of some time, the perfectly clear water is decanted off, and the mercury poured into a weighed porcelain crucible, where the greater portion of the water still adhering to it is removed with blotting-paper. The mercury is then finally dried under a bell-jar, over concentrated sulphuric acid, but without application of heat, until the weight remains constant. For the properties of the metal, see § 84. This method may be used also for the analysis of organic compounds of mercury. If properly and carefully executed, it gives accurate results. The most highly accurate results are, however, obtained by the application of the somewhat more complicated modification adopted by *Erdmann* and *Marchand* for the determination of the atomic weight of mercury and of sulphur. For the details of this modified process, I refer to the original essay in the "Journal für praktische Chemie," XXXI. p. 385; also "Pharmaceutisches Centralblatt," 1844, p. 354—simply remarking here, that the distillation is conducted, in a combustion tube, in a current of carbonic acid gas, and that the distillate is received in a bulb apparatus with one end filled with gold-leaf, to ensure the condensation of every trace of mercurial fumes. This way of receiving and condensing the fumes distilling over may be employed also in the analysis of amalgams, as recently done by *König* ("Journ. f. prakt. Chem." 70, 64).

b. In the Humid Way.

The solution, free from nitric acid, and mixed with free hydrochloric acid, is precipitated, in a flask, with an excess of a clear solution of protochloride of tin, containing free hydrochloric acid; the mixture is boiled for a short time, and then allowed to cool. After a time, the perfectly clear supernatant fluid is decanted from the metallic mercury, which, if the process has fully succeeded, will be found united into one globule; if this is the case, the globule of mercury may be washed at once by decantation, first with water acidulated with hydrochloric acid, and finally with pure water, which is then partly removed by blotting-paper, and the mercury afterwards dried and weighed as in *a*.

If, on the other hand, the particles of the mercury have not united, their union into one globule may readily be effected by boiling a short time with some moderately dilute hydrochloric acid (having, of course, previously removed by decantation the supernatant clear fluid). For the properties of metallic mercury, see § 84.

Phosphorous acid, sulphurous acid, and other reducing agents, may be substituted for the protochloride of tin.

This method gives accurate results, but it requires the *very greatest* care in performing the several operations. The resulting numbers are generally a little too low. (Compare Experiment No. 70, made by one of the students in my laboratory.) This, however, is entirely owing to defective execution of the operations, and by no means to defects inherent in the method itself; and the generally received notion, which would impute the deficiency to the volatilization of a portion of the mercury, in the processes of boiling and drying, is founded in error. (See Experiment No. 51.)

2. *Determination as Subchloride of Mercury.*

Mix the solution with hydrochloric acid, if that acid is not already present, add solution of soda or potassa until the excess of acid is *nearly* neutralized, mix with a solution of formate of soda in excess, and let the mixture stand four days, at a temperature of from 140° to 176° F. Filter the fluid off from the precipitated subchloride, and collect the latter on a weighed filter, dried at 212° F. Let the filtrate stand 24 hours longer, at a temperature of from 140° to 176° F., and, should a new precipitate form, add this to the first, and repeat the same process until the filtrate remains perfectly clear. Wash the collected precipitate, dry at 212° F., and weigh.

This method is very tedious, and requires, besides, the strictest attention in the performance of the several operations; its application is therefore almost exclusively confined to the separation of mercury from certain metals. The operator must take particular care not to exceed a temperature of 176° F., since otherwise metallic mercury might separate; should this be the case, the precipitate will exhibit a grayish appearance, and the experiment must, under such circumstance, be considered a failure.

3. *Determination as Sulphide of Mercury.*

a. The Solution of the Salt of Mercury is free from Nitric Acid.

Acidify the solution, if not already acid, slightly, with hydrochloric acid, transfer to a flask with ground stopper, and add a freshly prepared clear saturated solution of sulphuretted hydrogen in slight excess, just sufficient to make the odor of that gas clearly perceptible after shaking the flask; insert the stopper, and let the precipitated sulphide subside.

b. The amount of Mercury present is so considerable, that its Precipitation would require a very large portion of Sulphuretted Hydrogen Water.

Conduct into the moderately dilute solution washed sulphuretted hydrogen gas.

c. The Solution contains Nitric Acid.

Add solution of soda or potassa until the acid is *nearly* neutralized; mix the fluid with a clear solution of cyanide of potassium in excess, and precipitate the mercury finally, either with sulphuretted hydrogen water, or with colorless sulphide of ammonium, or by transmitting sulphuretted hydrogen gas through it. Let the precipitate subside, collect it on a weighed filter, wash rapidly with cold water, dry at 212° F., and weigh.

If the precipitate contains free sulphur (owing to the presence of sesquioxide of iron, chromic acid, &c. &c., or to some other cause), transfer it, still moist, together with the filter, to a small flask, treat with hydrochloric acid, apply a gentle heat, and add nitric acid, drop by drop, until the separated sulphur exhibits a pure yellow color; dilute the mixture now with water, filter, and precipitate again as sulphide, by addition of solution of soda or potassa, cyanide of potassium, and sulphuretted hydrogen gas, or sulphuretted hydrogen water, or colorless sulphide of ammonium, as above. For the properties of the precipitate, see § 84.

This method gives very accurate results, and is, in my opinion, preferable to all others.

4. *Determination as Oxide.*

In the salts of the oxides of mercury, with nitrogen acids, the metal may be determined in the form of oxide. For this purpose, the salt is heated in a bulb-tube, of which the one end, drawn out to a point, dips under water, the other end being connected with a gasometer, by means of which dry air is transmitted through the tube, as long as the application of heat is continued. In this way complete decomposition of the salt it effected, whilst the oxide to which it is reduced remains unaffected. (*Marignac*, in *Liebig* and *Kopp's* "Annual Report," 1849, page 594.)

5. *Volumetrical Analysis* (*Liebig's* method—"Annalen der Chemie und Pharmacie," 85, 307).

This method is based upon the circumstance that phosphate of soda precipitates mercury from solutions of the nitrate, but not from solutions of the chloride, in the form of a flocculent white precipitate, which speedily becomes crystalline; and that chloride of sodium, therefore, readily redissolves this precipitate (as long as it has not yet acquired crystalline consistence), phosphate of soda and chloride of mercury being formed. Consequently, if we know the quantity of chloride of sodium required to redissolve the precipitate, we learn from this also the quantity of the mercury; since every equivalent of chloride of sodium dissolves an equivalent of oxide of mercury (in the form of phosphate).

a. Preparation of the Solution of Chloride of Sodium.

The decimal equivalent solution of chloride of sodium (§ 115, 5) may be used. Every cubic centimetre of this containing 0·005846 grm. of Na Cl, corresponds to 0·010805 of Hg O.

b. Preparation of the Solution of Oxide of Mercury.

According to *Liebig*, this solution—which must, of course, be perfectly free from compounds of chlorine, iodine, and bromine, and in which all the mercury must be present in the state of oxide—should contain no more than about 0·2 grm. of oxide of mercury in 10 cubic centimetres of fluid. Accordingly, if a preliminary experiment shows it to have a higher degree of concentration, dilution to the proper degree must be resorted to. The solution must, moreover, contain no other metals besides mercury, nor too much free acid: the addition of from 3 to 4 cubic centimetres of a perfectly saturated solution of phosphate of soda to 10 cubic centimetres of the solution, must remove all acid reaction. If too much acid is present, carbonate of soda must be added until basic salt begins to precipitate, which latter is then redissolved by addition of one or two drops of nitric acid.

c. Performance of the Analytical Process.

There are two different methods recommended, which it is best to apply in combination, as the results obtained by the former are somewhat too high, those by the latter a little too low.

1. Measure off into a beaker, 10 cubic centimetres of the solution of oxide of mercury, add 3 or 4 cubic centimetres of a saturated solution of phosphate of soda, and then immediately, before the precipitate has had time to acquire crystalline consistence, solution of chloride of sodium, until the precipitate is just redissolved; the last

portions of the solution of chloride of sodium must be added very cautiously, to avoid addition in excess.

Supposing you have used 20·5 cubic centimetres of solution of chloride of sodium, to effect the precipitate of the solution formed upon the addition of the solution of phosphate of soda, you must now—

2. Measure off 20·5 c.c. of the same solution of chloride of sodium, add to this 3 or 4 cubic centimetres of solution of phosphate of soda, and then solution of oxide of mercury (*b*) from a burette, until a permanent precipitate just begins to form. Supposing this has taken 10·25 cubic centimetres of solution of mercury, then 20·5 + 20·5 = 41 cubic centimetres of solution of chloride of sodium having been consumed to 10 + 10·25 = 20·25 cubic centimetres of solution of oxide of mercury; and 1 cubic centimetre of the solution of chloride of sodium corresponding to 0·010805 grm. of oxide of mercury, it follows that 41 cubic centimetres of the chloride of sodium solution correspond to 0·443005 grm. of oxide of mercury, which quantity is consequently contained in 20·25 cubic centimetres of the analysed solution.

Liebig has proved by numerous experiments that this course of proceeding gives very nearly accurate results; he obtained, for instance, 0·1878 grm. instead of 0·1870 grm., 0·174 grm. instead of 0·1748 grm., 0·1668 grm. instead of 0·166 4 grm., &c. But the method is susceptible only of very limited application; for which reason I omit giving a description of *Fr. Mohr's* modification of the process, which consists in the substitution of ferricyanide of potassium for phosphate of soda (See *Fr. Mohr's* "Lehrbuch der Titrirmethode," 2, 66).

§ 119.

5. OXIDE OF COPPER.

a. Solution.

Most of the compounds of oxide of copper dissolve in water. Metallic copper is best dissolved in nitric acid. Oxide of copper, and those of its salts which are insoluble in water, may be dissolved in nitric acid, hydrochloric acid, or sulphuric acid. Sulphide of copper is heated with moderately dilute nitric acid, until the separated sulphur exhibits a pure yellow tint; addition of a little hydrochloric acid greatly promotes the decomposition.

b. Determination.

Copper may be weighed in the form of *oxide*, or in the *metallic* state, or as *subsulphide* (§ 85). Into the form of oxide it is converted either by *direct* precipitation, or by ignition, or after previous precipitation as *sulphide.* The determination as subsulphide is preceded by precipitation either as sulphide or as sulphosubcyanide. Copper may be determined also in an indirect way, and by volumetrical analysis.

We may convert into

1. OXIDE OF COPPER.

a. By direct Precipitation as Oxide.

All salts of oxide of copper soluble in water, and also those of the insoluble salts of which the acids may be removed upon solution in nitric acid, provided no non-volatile organic substances be present.

b. By Precipitation, preceded by Ignition of the Compound.

Such of the salts enumerated sub *a* as contain a non-volatile organic substance, and thus more particularly salts of copper with non-volatile organic acids.

c. By Precipitation as Sulphide of Copper.

All compounds of copper without exception.

d. By Ignition.

Salts of copper with readily volatile oxygen acids, or with such oxygen acids as are readily decomposed at a high temperature (carbonate of copper, nitrate of copper).

2. METALLIC COPPER.

Oxide of copper in all solutions free from metals precipitable by zinc.

3. SULPHO-SUBCYANIDE OF COPPER, resp. SUBSULPHIDE OF COPPER.

Oxide of copper in all cases in which no other metals precipitable by sulphocyanide of potassium are present.

Of the several methods of effecting the quantitative estimation of copper, I prefer in all cases where the choice is left free and where precipitation cannot be avoided, method 2, as the process is more rapidly performed than is the case with method 1, while the results are, at least, equally accurate. Method 3 finds application chiefly in separations of copper from other metals. The volumetrical methods are especially adapted for technical purposes, but they are inferior to method 2 in simplicity and accuracy. For technical purposes, there are, besides the volumetrical, also several colorimetrical methods, proposed by *Heine, Von Hubert, Jacquelain, A. Müller*, and others, which are, all of them, based upon the comparison of an ammoniacal solution of oxide of copper, of any indefinite standard, with others of a known standard. See *Al. Müller's* "Complementärcolorimeter" Chemnitz, 1854 ; and *Bodemann's* "Probirkunt," *von Kerl*, page 222.

Levol's indirect method of estimating copper, which is based upon the diminution of weight suffered by a strip of copper when digested in a close-stoppered flask with ammoniacal solution of copper and water boiled free from air, the decolorization of the fluid marking the completion of the reaction, takes too much time, and is apt to give false results (*Phillip's*, "Annal. d. Chem. u. Pharm.," 81, 208). The latter remark applies also to the indirect method proposed by *Runge*, which consists in boiling the solution of copper, free from nitric acid and sesquioxide of iron, in presence of some free hydrochloric acid, in a flask, with a weighed strip of copper, and, after decolorization of the fluid, determining the loss of weight suffered by the copper.

1. *Determination as Oxide of Copper.*

a. By direct Precipitation as Oxide.

α. From Neutral or Acid Solutions.

Heat the *rather dilute* solution in a platinum or porcelain dish, to incipient ebullition, add a somewhat dilute solution of pure soda or potassa until the formation of a precipitate ceases, and keep the mixture a few minutes longer at a temperature near boiling.

After allowing some time for the subsidence of the precipitate, filter off the fluid, treat the precipitate with water, heat to boiling, let the precipitate somewhat subside, and repeat the operation just described once or twice. Collect the whole of the precipitate finally on the filter, wash thoroughly with hot water, dry, and ignite in a platinum crucible, as directed § 53. After intense ignition, and having added the ash of the filter, let the crucible and its contents cool under a bell-jar, over concentrated sulphuric acid, place it on the balance the instant it is cold, and weigh as quickly as possible. The action of reducing gases must be carefully guarded against in the process of ignition.

It will sometimes happen, though mostly from want of proper attention to the directions here given, that particles of the oxide of copper adhere so tenaciously to the dish that mechanical appliances fail to remove them. In a case of this kind you need simply wash the dish thoroughly, dissolve the adhering particles with a few drops of nitric acid, and evaporate the solution over the principal mass of the precipitated oxide, before you proceed to ignite the latter. Should the solution be rather copious, it must first be concentrated by evaporation, until only *very little* of it is left. For the properties of the precipitate, see § 85.

With proper attention to the directions here given, most accurate results are attained by this method; deviations from these directions will impair more or less the accuracy of the results. Thus, if the solution be not sufficiently dilute, the precipitant will fail to throw down the whole of the oxide of copper; or, if the precipitate be not thoroughly washed with hot water, it will retain a portion of the alkali; or, if the ignited precipitate be allowed to stand exposed to the air, before it is weighed, an increase of weight will be the result; and so, on the other hand, a diminution of weight, if the filter be ignited in contact with the oxide, since this will, of course, tend to reduce it more or less. Should a portion of the oxide have suffered reduction, it must be reoxidized by moistening with nitric acid, evaporating cautiously to dryness, and exposing the residue to a gentle heat, increasing this gradually to a high degree of intensity.

Let it be an invariable rule to test the filtrate for copper with sulphuretted hydrogen water. If, notwithstanding the strictest compliance with the directions here given, the addition of this reagent produces a precipitate, or imparts a brown tint to the fluid, this is to be attributed to the presence of organic matter; in that case, concentrate the filtrate and washing water by evaporation, precipitate with sulphuretted hydrogen water, treat the precipitated sulphide as directed in *c*, and add the oxide obtained to the first precipitate. It is also highly advisable not to neglect dissolving the oxide of copper, after weighing, in hydrochloric acid, in order to detect, and, if necessary, estimate, any silicic acid which might be present.

β. From Alkaline Solutions.

From ammoniacal solutions also, oxide of copper may be precipitated by soda or potassa. In the main, the process is conducted as in *α*. After precipitation the mixture is heated, until the fluid above the precipitate has become perfectly colorless; the fluid is then filtered off with the greatest possible expedition. If allowed to cool with the precipitate in it, a small portion of the latter would redissolve.

b. By Precipitation as Oxide, preceded by Ignition of the Substance under Examination.

Heat the substance in a porcelain crucible, until the organic matter present is totally destroyed; dissolve the residue in dilute nitric acid, filter, if necessary, and treat the clear solution as directed in *a*, *α*, or evaporate it, and treat the residue as in *d*.

c. By Precipitation as Sulphide of Copper.

Precipitate the solution—which may be alkaline, neutral, or slightly acid, but should not contain a great excess of nitric acid—according to the smaller or larger quantity of copper present, either with strong sulphuretted hydrogen water, or by conducting sulphuretted hydrogen gas into it. When the precipitate has fully subsided, and you have made sure that the supernatant fluid is no longer colored or precipitated by strong *sulphuretted hydrogen water*, filter off quickly, wash the precipitate without intermission with water impregnated with sulphuretted hydrogen, and dry on the filter with some expedition; transfer the dried precipitate to a beaker, incinerate the filter in a small porcelain dish, add the ash to the precipitate, treat with moderately dilute nitric acid, add some hydrochloric acid, and heat gently until the separated sulphur appears of a pure yellow color; dilute now with water, filter, and precipitate as directed in *a*.

Instead of precipitating the copper, as sulphide, with hydrosulphuric acid, or an alkaline sulphide, it may also be precipitated with hyposulphite of soda. To this end, the solution of copper, which, if necessary, must, by evaporation with sulphuric acid, be freed as far as practicable from hydrochloric acid and nitric acid, is sufficiently diluted, heated to boiling, and mixed with a solution of hyposulphite of soda, as long as a black precipitate forms. As soon as this black precipitate has subsided, leaving only suspended sulphur in the supernatant fluid, the precipitation of the copper is complete. The precipitate is subsulphide of copper (Cu_2S); it may easily be washed without risk of oxidation (*Flajolot*, "Journ. f. prakt. Chem.," 61, 105). It is finally converted into oxide as directed in 1, *a*.

Instead of converting the sulphide or subsulphide of copper into oxide, it may also be collected in a small boat, and ignited in a tube, through which a current of hydrogen gas is transmitted. By this process pure subsulphide of copper is produced (*Berzelius; Brunner*).

d. By Ignition.

The salt is put into a platinum or porcelain crucible, and exposed to a very gentle heat, which is gradually increased to intense redness; the residue is then weighed.

As nitrate of copper spurts strongly when ignited, it is always advisable to put it into a small covered platinum crucible, and to place the latter in a large one, also covered. With proper care, the results are very accurate. Copper salts with organic acid also may be converted into oxide by simple ignition. To this end, the residue first obtained, which contains suboxide, is completely oxidized, by repeated moistening with nitric acid, and ignition. However, a trifling loss of substance is generally incurred in this process, from the difficulty of avoiding spurting.

2. Determination as Metallic Copper.

The method of precipitating copper with iron or zinc, and weighing it in the metallic state, was proposed as far back as 1822, in *Pfaff's*[*]

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[*] I mention this fact as I think it would be most unjust to *Pfaff* to attribute to *Kerl* the method of precipitating copper with iron, and to *Mohr* that of precipitating it with zinc. I feel called upon to make this remark in reference to *Fr. Mohr's* paper on the subject, in "Annal. d. Chem. u. Pharmacie," 96, 215, and *Bodemann's* "Probirkunst," von *Kerl*, page 220.

"Handbuch der analytischen Chemie," Altona, 1822, vol. 2, page 269, where the reasons are given for preferring zinc as the precipitant, and sulphuretted hydrogen is recommended as a test for ascertaining whether the precipitation is complete.

The method has been in use in my laboratory now for three years, with the most satisfactory results. From my own experience I can recommend the following process as best suited to effect the object in view.

Introduce the solution of copper, after having, if required, first freed it from nitric acid, by evaporation with hydrochloric acid or sulphuric acid, into a weighed platinum dish; dilute, if necessary, with some water, throw in a piece of zinc, soluble in hydrochloric acid without residue, and add, if necessary, hydrochloric acid in sufficient quantity to produce a moderate evolution of hydrogen. If, on the other hand, this evolution should be too brisk, owing to an over-large excess of acid, add a little water. Cover the dish with a watch-glass, which is afterwards rinsed into the dish with the aid of a washing-bottle. The separation of the copper begins immediately; a large proportion of it is deposited on the platinum in form of a solid coating; another separates more particularly from concentrated solutions in the form of red spongy masses. Application of heat, though it promotes the reaction, is not necessary; but there must always, throughout the process, be sufficient free acid present to keep up the evolution of hydrogen. After the lapse of about an hour or two, the whole of the copper has separated. To make sure of this, test a small portion of the supernatant fluid with sulphuretted hydrogen water; if this fails to impart a brown tint to it, you may safely assume that the precipitation of the copper is complete. Ascertain now, also, whether the zinc is entirely dissolved, by feeling about with a glass rod whether it encounters any hard lumps, and observing whether renewed evolution of hydrogen will take place upon addition of some hydrochloric acid. If the results are satisfactory in this respect also, decant the clear fluid, which is an easy operation, pour, without loss of time, boiling water into the dish, decant again, and repeat this operation until the washings are *quite* free from hydrochloric acid. Decant the water now as far as practicable, remove the rest by means of blotting paper, place the dish in a drying closet, heated to 212° F., and, when the copper is perfectly dry, let it get cold, and weigh. If you have no platinum dish, the precipitation may be effected also in a porcelain crucible or glass dish; but it will, in that case, take a longer time to accomplish it, owing to the absence of the galvanic antagonism between platinum and zinc; and the whole of the copper will be obtained in loose masses, and not firmly adhering to the sides of the crucible or dish, as in the case of precipitation in platinum vessels.

The results are very accurate. Direct experiment, No. 71, gave 100·0 and 100·06, instead of 100. *Fr. Mohr* ("Annal. d. Chem. u. Pharm.," 96, 215) effected the precipitation in a porcelain crucible, and obtained equally satisfactory results.

3. *Precipitation as Sulpho-subcyanide of Copper.*

(*Rivot's* process, "Compt. rend.," 38, 868. "Journ. f. prakt. Chem.," 62, 252.)

Make a solution of the compound of copper in hydrochloric acid, taking care to exclude oxidizing substances; mix the solution with a sufficient quantity of sulphurous or hypophosphorous acid, and add a solution of sulphocyanide of potassium. The copper precipitates immediately, and completely, as white sulpho-subcyanide of copper. Collect the precipitate on a weighed filter, wash with water, dry at 212° F., and weigh. This gives already very approximate results; direct experiment, No. 72, gave 99·66, instead of 100. However, as the precipitate may still retain water, introduce a weighed aliquot part of it in a small porcelain boat; mix with some sulphur, insert the boat in a glass tube, transmit hydrogen gas through the latter, and apply heat until the excess of sulphur is expelled; weigh the subsulphide of copper ($Cu_2 S$), and repeat the ignition with sulphur until the weight remains constant. The total amount of subsulphide of copper which the whole precipitate would yield if subjected to the same process, is calculated from the quantity found. *Rivot* directs the ignition to be conducted in a porcelain crucible; from this I totally dissent. For the properties of sulpho-subcyanide and subsulphide of copper, see § 85.

4. *Volumetrical Methods.*

a. *Schwarz's* Method ("Annal. der Chemie und Pharm.," 84, 84).

If a solution of oxide of copper is mixed with a sufficient quantity of a tartrate of an alkali, and solution of soda added, a deep blue fluid is produced. If this is warmed, and a sufficient amount of grape-sugar added, the whole of the copper precipitates, after a short time, in the form of suboxide. On warming this with sesquichloride of iron and hydrochloric acid, it dissolves, the following transposition taking place:

$$Cu_2 O + Fe_2 Cl_3 + H Cl = 2 Cu Cl + 2 Fe Cl + H O.$$

Each equivalent of copper consequently reduces one equivalent of iron from the state of sesquichloride to that of protochloride. From the quantity obtained of the latter, we may accordingly ascertain the amount of the copper.

The analytical process is conducted as follows:—Dissolve the weighed compound of copper under examination in water or nitric acid, in a capacious porcelain dish, mix in the cold, with a solution of neutral tartrate of potassa, and add solution of potassa or soda in excess. Mix the dark blue fluid now with a sufficient quantity of an aqueous solution of grape-sugar or milk-sugar, and warm on the water-bath, until the fluid shows a brown color on the border, which is a sign that the whole of the copper is precipitated, and that the potassa begins to act upon the sugar, imparting a brown tint to it. When the precipitate has subsided, filter. The filtrate appears, in most cases, of a deep brown color; upon the addition of the washing water, a muddy yellowish layer forms at the surface of contact; however, this disappears immediately upon stirring the fluid—a proof that it does not proceed from any suboxide of copper having passed through the filter. Wash the precipitated suboxide of copper with hot water, until the washing water comes off perfectly colorless; particles of the suboxide adhering firmly to the dish are left in the latter. Put the filter, with the suboxide into the dish, add solution of pure sesquichloride of iron (free from nitric acid, chlorine, and protochloride) in slight excess, and a little hydrochloric acid, and heat gently, with stirring, which will suffice to redissolve the subchloride of copper at first formed. Filter the green solution into a capacious flask, wash the remains of the first filter thoroughly with hot water; let the fluid cool down to about 77° F., and estimate the quantity of protochloride of iron formed, as directed § 112,2. Every 28 parts of iron found in the state of protoxide of protochloride correspond to 31·68 parts of copper. The results are satisfactory. Direct experiments gave 99·4 and 100·2, instead of 100.

Fr. Mohr ("Lehrbuch der Titrirmethode," page 202) dissolves the suboxide of copper in hydrochloric acid, instead of solution of sesquichloride of iron and hydrochloric acid, and adds a pretty large proportion of chloride of sodium, dilutes, and determines the strength of the solution of subchloride of copper, without removing the filter. He obtained 98·57 and 98·68 instead of 100. The experiments made in my own laboratory, in the same way, gave 98·08 and 99·03, instead of 100. The reason why this method is so apt to give inaccurate results is, that a hydrochloric acid solution of subchloride of copper attracts oxygen much more rapidly than is the case with a solution of protochloride of iron. I cannot regard, therefore, *Mohr's* modification in the light of an improvement of *Schwarz's* method.

b. Fleitmann's method ("Annal. d. Chem. u. Pharm.," 98, 141).

If you have an acid solution, free from nitric acid, precipitate the copper with zinc, exactly as directed in 2, digest with dilute sulphuric acid until the zinc is completely dissolved, removing any iron which the solution may have contained, by thorough washing of the copper, and add solution of sesquichloride of iron and hydrochloric acid. The copper dissolves speedily, giving two equivalents of protoxide of iron. Dilute, and determine with solution of permanganate of potassa. 56 of iron, which are present as protoxide, correspond to 31·68 of copper. It is quite evident that this method of determining copper will be found more convenient than method 2 only in cases where the operator has to make a whole series of analyses. The results, obtained in an indirect way, can never attain the accuracy which the direct weighing of copper affords; still the difference generally does not exceed 1 per cent.

If the solution contains nitric acid or metals reducible by zinc (*e. g.*, teroxide of bismuth, oxide of lead), the precipitation is effected in the ammoniacal solution of copper—which must be filtered, if necessary—by warming it moderately with fine zinc raspings or filings, until the blue color of the fluid has disappeared, and the copper is completely precipitated. The precipitated copper is first thoroughly washed with hot water, then digested with dilute sulphuric acid to remove the excess of zinc, after this washed again with water, and treated finally as directed above.

c. De Haen's method ("Annal. d. Chem. u. Pharm.," 91, 237).

I recommend this method, which was devised in my own laboratory, as more especially applicable in cases where small quantities of copper are to be estimated in an expeditious way. The method is based upon the fact that, when a salt of oxide of copper in solution is mixed with iodide of potassium in excess, subiodide of copper and free iodine are formed, the latter remaining dissolved in the solution of iodide of potassium: $2\,(CuO, SO_3) + 2\,KI = Cu_2I + 2\,KO, SO_3 + I$. Now, by estimating the iodine by *Bunsen's* method (§ 145), we learn the quantity of copper. The following is the most convenient way of proceeding. Dissolve the compound of copper in sulphuric acid, best to a neutral solution; a moderate excess of free sulphuric acid, however, does not injuriously affect the process. Dilute the solution, in a measuring flask, to a definite volume; 100 cubic centimetres should contain from 1 to 2 grammes of oxide of copper. Introduce now about 10 cubic centimetres of *Bunsen's* iodide of potassium solution into a large beaker, add 10 cubic centimetres of the copper solution, mix, add, without loss of time, sulphurous acid, and proceed as directed in § 145. The copper solution must contain no sesquioxide of iron or other bodies which decompose iodide of potassium, nor free nitric acid, or free hydrochloric acid; no time must be lost in adding the sulphurous acid, as this would impair the accuracy of the results. With strict attention to these rules, the results are accurate. *De Haen* obtained, for instance, 0·3567 instead of 0·3566 of sulphate of copper, 99·98 and 100·1 instead of 100 of metallic copper. Further experiments (No. 73) have convinced me, however, that, though the results attainable by this method are satisfactory, they are not always quite so accurate as would be supposed from the above figures given by *De Haen.* Acting upon *Fr. Mohr's* suggestion, I tried to counteract the injurious influence of the presence of nitric acid, by adding to the solution containing nitric acid first ammonia in excess, then hydrochloric acid to slight predominance; the result was by no means satisfactory. The reason of this is that a solution of nitrate of ammonia, mixed with some hydrochloric acid, will, even after a short time, begin to liberate iodine from solution of iodide of potassium.

d. Carl Mohr's method (*Fr. Mohr's* Lehrbuch der Titrirmethode 2, 91). The principle of this method is as follows: If solution of cyanide of potassium is added, drop by drop, to an ammoniacal solution of copper, the azure blue color disappears gradually, and the fluid at last becomes colorless, or, rather, faint yellowish. $Cu_2 Cy, N H_4 Cy$ and $K O$ are formed; the one-half of cyanogen, which is eliminated in the process, produces by its action upon the free ammonia, urea, oxalate of urea, cyanide of ammonium, and formate of ammonia (*Liebig,* "Annal. d. Chem. u. Pharm.," 95, 118). The decomposition is not uniform under all circumstances and conditions; on the contrary, the quantity and concentration of the ammonia exercise considerable influence upon it. Experiments of my own have fully confirmed the truth of this remark of *Liebig,* and have shown, moreover, that presence of neutral salts of ammonia alters the results (see experiment No. 74). The method, though unquestionably very convenient, is, therefore, unfortunately, susceptible of but limited application, and its results can be relied upon in few cases only. The standard solution of cyanide of potassium intended to effect the quantitative estimation of the copper in the compound under examination is determined by means of a solution of copper of known strength. The process is conducted in a porcelain dish; the completion of the reaction is sufficiently marked and distinct. Other metals of which the oxides dissolve in ammonia, *e. g.,* zinc, must not be present; arsenious and arsenic acids are without influence.

e. Besides the foregoing volumetrical methods, several others have been proposed. However, as they are still less reliable, I dismiss them here with a mere passing allusion.

α. *Pelouze's* method (see second English edition, page 199). It is difficult to mark the completion of the reaction; the results are therefore apt to differ to the extent of several per cent.

β. Another method by *Carl Mohr* ("Annal. d. Chem. u. Pharm.," 92, 97). Reduction of the slightly acid solution of copper by iron, and estimation of the protoxide of iron formed gives unreliable results; often 12 per cent. and more too high.

γ. *Leeshing's* method ("Journ. f. prakt. Chem.," 61, 376). Precipitation with oxalate of potassa.

§ 120.

6. TEROXIDE OF BISMUTH.

a. Solution.

Metallic bismuth, the teroxide, and all other compounds of that metal, are dissolved best in more or less dilute nitric acid.

b. Determination.

Bismuth is weighed in the form of *teroxide* or as *chromate of teroxide.* The compounds of bismuth are converted into teroxide, either by ignition, or by precipitation as *basic carbonate of teroxide of bismuth,* preceded in some cases by precipitation as *tersulphide.*

We may convert into

1. TEROXIDE OF BISMUTH.

a. By Precipitation as Carbonate of Teroxide of Bismuth.

All compounds of bismuth which dissolve in nitric acid to nitrate, no other acid remaining in the solution.

b. By Ignition.

α. Salts of bismuth with readily volatile oxygen acids.

β. Salts of bismuth with organic acids.

c. By Precipitation as Tersulphide of Bismuth.

All compounds of bismuth without exception.

2. CHROMATE OF TEROXIDE OF BISMUTH.

All compounds named in 1, *a.*

1. *Determination of Bismuth as Teroxide.*

a. By Precipitation as Carbonate of Teroxide of Bismuth.

Mix the solution of bismuth with carbonate of ammonia in *very slight* excess, and heat for a short time nearly to boiling; filter, dry the precipitate, and ignite in the manner directed § 116 (ignition of carbonate of lead); the process of ignition serves to convert the carbonate into the pure teroxide of bismuth. Should the solution be too concentrated, dilute with water, previously to the addition of carbonate of ammonia; whether the dilution leads to the precipitation of basic nitrate of bismuth or not, is a matter of perfect indifference. For the properties of the precipitate and residue, see § 86.

The method gives accurate results, though generally a trifle too low, owing to the circumstance that carbonate of teroxide of bismuth is not absolutely insoluble in carbonate of ammonia.

Were you to attempt to precipitate bismuth, by means of carbonate of ammonia, from solutions containing sulphuric acid or hydrochloric acid, you would obtain incorrect results, since the teroxide would contain, in the former case, an admixture of basic sulphate, in the latter, of basic terchloride of bismuth. Were you to filter off the precipitate, without previous application of heat, part of the basic carbonate would remain in solution, which would, of course, considerably reduce the resulting numbers (experiment No. 75).

b. By Ignition.

α. Compounds like the carbonate or nitrate of teroxide of bismuth are ignited in a porcelain crucible until their weight remains constant.

β. Compounds of teroxide of bismuth with organic acids are treated like the corresponding compounds of oxide of copper (§ 119, 1, *d.*).

c. By Precipitation as Tersulphide of Bismuth.

Dilute the solution with water slightly acidulated with acetic acid (to prevent the precipitation of a basic salt), and precipitate with sulphuretted hydrogen water or gas; allow the precipitate to subside, and test a portion of the supernatant fluid with *sulphuretted hydrogen water;* if it remains clear, which is a sign that the bismuth is completely precipitated, filter, and wash the precipitate. Or mix with ammonia until the free acid is neutralized, and then add sulphide of ammonium in excess.

The tersulphide of bismuth may be weighed in that form, if the operator is convinced that no free sulphur has been thrown down in conjunction with it. But, as in the case of compounds of bismuth we have mostly to deal with very acid solutions, and which contain nitric acid, there is generally reason to apprehend a partial decomposition of the sulphuretted hydrogen, attended with separation of free sulphur, on which account it is always safest to convert the tersulphide into teroxide. To this end the filter, with the washed and still moist precipitate on it, is put into a beaker, and heated with moderately strong nitric acid until complete decomposition is effected; the solution is then diluted with water slightly acidulated with acetic or nitric acid, and filtered, the filter being washed with the acidulated water; the filtrate is then finally precipitated as directed in *a.*

2. *Determination of Bismuth as Chromate of Teroxide* (*J. Löwe's* method, "Journ. f. prakt. Chem.," 67, 464).

Pour the solution of teroxide of bismuth, which must be as neutral as possible, and must, if necessary, be first freed from the excess of nitric acid by evaporation on the water-bath, into a warm solution of pure bichromate of potassa, in a porcelain dish, with stirring, and take care to leave the alkaline chromate slightly in excess. Rinse the vessel which contained the solution of bismuth with water containing nitric acid, and add the rinsings to the contents of the porcelain dish. The precipitate formed must be orange-yellow, and dense throughout; if it is flocculent, and has the color of the yolk of an egg, this is a sign that there is a deficiency of chromate of potassa; in which case add a fresh quantity of this salt, taking care, however, to guard against too great an excess, and boil until the precipitate presents the proper appearance. Boil the contents of the dish for ten minutes, with stirring; then wash the precipitate, first by repeated boiling with water and decantation on to a weighed filter, at last thoroughly on the latter with boiling water, dry at about 248° F., and weigh. For the properties and composition of the precipitate, see § 86.* Results very satisfactory.

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* *Pearson* ("Phil. Mag.," xi. 204) gives $Bi\,O_3, Cr\,O_3$ as the formula of the precipitate, and, at the same time, 1 grm. of bismuth in 1·491 of chromate of teroxide, which involves a contradiction. Both statements are erroneous. His volumetrical estimation is based upon the mistaken assumption that chromate of teroxide of bismuth is insoluble in dilute nitric acid, whilst it is only so in presence of a sufficient excess of chromate of potassa.

§ 121.

7. OXIDE OF CADMIUM.

a. Solution.

Cadmium, its oxide, and all the other compounds insoluble in water, are dissolved in hydrochloric acid or in nitric acid.

b. Determination.

Cadmium is weighed either in the form of *oxide*, or in that of *sulphide* (§ 87).

We may convert into

1. OXIDE OF CADMIUM.

a. By Precipitation.

The compounds of cadmium which are soluble in water; the insoluble compounds, the acid of which is removed upon solution in hydrochloric acid; salts of cadmium with organic acids.

b. By Ignition.

Salts of cadmium with readily volatile or easily decomposable inorganic oxygen acids.

2. SULPHIDE OF CADMIUM.

All compounds of cadmium without exception.

1. *Determination as Oxide of Cadmium.*

a. By Precipitation.

Precipitate with carbonate of soda or potassa, wash the precipitated carbonate of cadmium, and reduce it, by ignition, to the state of pure oxide. For the details of the method of proceeding, and the accuracy of the results, I refer to § 108 (Zinc). For the properties of the precipitate and residue, see § 87.

b. By Ignition.

See § 108, *c* (Zinc).

2. *Determination as Sulphide of Cadmium.*

Precipitate the solution, if neutral or acid, with sulphuretted hydrogen water or gas—if alkaline, with sulphide of ammonium; collect the precipitate on a weighed filter, wash, dry at 212° F., and weigh. For the properties of the precipitate, see § 87. The results are accurate.

Should the precipitated sulphide of cadmium contain an admixture of free sulphur, it must be converted into nitrate or chloride of cadmium, and subsequently precipitated as carbonate of cadmium, in the manner directed, § 108 (Zinc). The precipitation of sulphur along with the sulphide of cadmium may often be prevented, by adding to the solution of cadmium cyanide of potassium until the precipitate formed is redissolved, and then precipitating the solution with sulphuretted hydrogen.

Supplement to the Fifth Group.

§ 122.

8. PROTOXIDE OF PALLADIUM.

Protoxide of palladium is reduced to the metallic state for the purpose of effecting its quantitative estimation. This may be done in several ways.

a. Neutralize the solution of protochloride of palladium almost completely with carbonate of soda, mix with a solution of cyanide of mercury; and digest the mixture for some time. A yellowish-white precipitate of protocyanide of palladium will subside, from dilute solutions, only after the lapse of some time. Wash this precipitate, dry, and ignite; weigh the reduced metal obtained. If the solution contains nitrate of protoxide, evaporate it first with hydrochloric acid to dryness; as the precipitate obtained from a solution of the kind deflagrates upon ignition (*Wollaston*).

b. Mix the solution of the protochloride or nitrate of protoxide of palladium with formate of soda or potassa, and warm until no more carbonic acid escapes. The palladium precipitates in brilliant scales (*Döbereiner*).

c. Precipitate the acid solution of palladium with sulphuretted hydrogen, filter, wash with boiling water, roast, and either convert the basic sulphate of protoxide of palladium formed into pure metal, by ignition over the blast gas-lamp, or dissolve it in hydrochloric acid, and precipitate as in *a.*

Exposed to a moderate red heat *metallic palladium* becomes covered with a film varying from violet to blue, but at a higher temperature it recovers its lustre; this tarnishing and recovery of the metallic lustre is not attended with any perceptible difference of weight. Palladium requires the very highest degree of heat for its fusion. It dissolves readily in nitrohydrochloric acid, with difficulty in pure nitric acid, more easily in nitric acid containing nitrous acid, with difficulty in boiling hydrated sulphuric acid.

SIXTH GROUP OF THE BASES.

TEROXIDE OF GOLD—BINOXIDE OF PLATINUM—TEROXIDE OF ANTIMONY—BINOXIDE OF TIN—PROTOXIDE OF TIN—ARSENIOUS AND ARSENIC ACIDS—(MOLYBDIC ACID).

§ 123.

I. TEROXIDE OF GOLD.

a. Solution.

Metallic gold, and all compounds of gold insoluble in water, are warmed with hydrochloric acid, and nitric acid is gradually added until complete solution is effected; or they are repeatedly digested with strong chlorine water. The latter method is resorted to more especially in cases where the quantity of gold to be dissolved is small, and mixed up with other oxides, which it is wished to leave undissolved.

b. Determination.

Gold is always weighed in the metallic state, to which its compounds are reduced by direct precipitation, or by ignition, preceded, in some cases, by precipitation as tersulphide of gold.

We may convert into

METALLIC GOLD.

a. By Ignition.	*b. By Precipitation as Metallic Gold.*
All compounds of gold which contain no fixed acid.	All compounds of gold without exception in cases where *a* is inapplicable.

c. By Precipitation as Tersulphide of Gold.

This method serves to effect the separation of gold from certain other metals which may be mixed with it in a solution.

Determination as Metallic Gold.

a. By Ignition.

Heat the compound, in a covered porcelain or platinum crucible, very gently at first, but finally to redness, and weigh the residuary pure gold. For properties of the residue, see § 88. The results are most accurate.

b. By Precipitation as Metallic Gold.

α. The solution is free from Nitric Acid.

Mix the solution with a little hydrochloric acid, if it does not already contain some of that acid in the free state, and add a clear solution of sulphate of protoxide of iron in excess; heat gently for a few hours until the precipitated fine gold powder has completely subsided; filter, wash, dry, and ignite (§ 52). A porcelain dish is a more appropriate vessel to effect the precipitation in than a beaker, as the heavy fine gold powder is more readily rinsed out of the former than out of the latter. The results are accurate.

β. The solution of Gold contains Nitric Acid.

Evaporate the solution, on a water-bath, to the consistence of syrup, adding from time to time hydrochloric acid; dissolve the residue in water containing hydrochloric acid, and treat the solution as directed in *α*. It will sometimes happen that the residue does not dissolve to a clear fluid, in consequence of a partial decomposition of the terchloride of gold into protochloride and metallic gold; however, this is a matter of perfect indifference.

γ. In cases where it is wished to avoid the presence of iron in the filtrate, the gold may be reduced by means of oxalic acid. To this end, the solution—freed previously, if necessary, from nitric acid, in the manner directed in *β*—is mixed, in a beaker, with oxalate of ammonia in excess, some hydrochloric acid added (if that acid is not already present in the free state), and the vessel, covered with a glass plate, is kept standing for two days in a moderately warm place. At the end of that time, the whole of the gold will be found to have separated in small yellow scales; the supernatant fluid is filtered off from the gold, which is then washed, dried, and ignited.

c. By Precipitation as Tersulphide of Gold.

Sulphuretted hydrogen gas is transmitted in excess through the dilute solution of the compound under examination; the precipitate formed is speedily filtered off, without heating, washed, dried, and ignited in a porcelain or platinum crucible. For the properties of the precipitate, see § 88. The results are accurate.

§ 124.

2. BINOXIDE OF PLATINUM.

a. Solution.

Metallic platinum, and the compounds of platinum which are insoluble in water, are dissolved by digestion, at a gentle heat, with nitrohydrochloric acid.

b. Determination.

Platinum is invariably weighed in the pure metallic state, to which its compounds are reduced, either by precipitation as *bichloride of platinum and chloride of ammonium*, or as *bichloride of platinum and chloride of potassium*, or as *bisulphide of platinum*, or by ignition, or by precipitation with reducing agents. All compounds of platinum, without exception, may, in most cases, be reduced to the metallic state by either of these methods. Which is the most advantageous process to be pursued in special instances, depends entirely upon the circumstances of particular cases. The reduction of compounds of platinum to the metallic state by simple ignition is preferable to the other methods, in all cases where its application is admissible. The precipitation as bisulphide of platinum is resorted to exclusively to effect the separation of platinum from other metals.

Determination as Metallic Platinum.

a. By Precipitation as Bichloride of Platinum and Chloride of Ammonium.

Mix the solution, in a beaker, with ammonia until the excess of acid (that is, supposing an excess of acid to be present) is *nearly* saturated; add chloride of ammonium in excess, and mix the fluid with a pretty large quantity of absolute alcohol. Should your solution of platinum be very dilute, you must concentrate it previously to the addition of the ammonia.

Cover the vessel now with a glass plate, and let it stand for twenty-four hours, after which filter on an unweighed filter, wash the precipitate thoroughly with spirit of wine of about 80 per cent., and dry carefully.

Introduce the dry precipitate, wrapped up in the filter, into a weighed porcelain or platinum crucible, put on the lid, and apply a very gentle heat until no more fumes of chloride of ammonium escape; now remove the lid, place the crucible obliquely (§ 41), and incinerate the filter. Apply finally an intense heat for some time, and then weigh the residue. For the properties of the precipitate and residue, see § 89. The results are satisfactory, though generally a little too low, as the bichloride of platinum and chloride of ammonium is not altogether insoluble in spirit of wine (Experiment No. 15); and as the fumes of chloride of ammonium evolved during the first stage of the process of ignition are liable to carry away traces of the yet undecomposed double chloride, if the application of heat is not conducted with the greatest possible care.

If the precipitated bichloride of platinum and chloride of ammonium were weighed in that form, the results would be inaccurate, since, as I have convinced myself by direct experiments, it is impossible to completely free the double chloride, by washing with spirit of wine, from all traces of the chloride of ammonium thrown down in conjunction with it, without dissolving, at the same time, a considerable portion of the double chloride. As a general rule, however, the results obtained by weighing the bichloride of platinum and chloride of ammonium in that form are one or two per cent. too high.

b. By Precipitation as Bichloride of Platinum and Chloride of Potassium.

Mix the solution of the compound under examination, in a beaker, with potassa, until the greater part of the excess of acid (if there be any) is neutralized; add chloride of potassium slightly in excess, and finally a pretty large quantity of absolute alcohol; should your solution of platinum be very dilute, you must concentrate it previously to the addition of the alcohol. Let the mixture stand for twenty-four hours, after which filter. Collect the precipitate upon a weighed filter, wash with spirit of wine of 70 per cent., dry thoroughly at 212° F., and weigh. Now put a portion of the dried precipitate into a weighed bulb-tube, and clean the ends of the latter with the beard of a feather; then weigh the tube again, to ascertain the exact amount of bichloride of platinum and chloride of potassium which it contains. Connect the tube now with an apparatus evolving dry hydrogen gas (Fig. 63), and heat its contents to redness, until no more hydrochloric acid fumes are evolved, which you may readily ascertain by holding a glass rod moistened with ammonia to the opening of the tube. Let the contents of the bulb cool, remove the tube from the apparatus, fill it with water, decant the solution of chloride of potassium cautiously, wash the residuary platinum carefully, dry the tube thoroughly, by heating it in a stream of hydrogen gas, and weigh. Subtract from the weight found the original weight of the empty tube, and calculate from the remainder (the weight of the residuary platinum in the tube) the amount of platinum contained in the precipitate of the bichloride of platinum and chloride of potassium.

For the properties of the precipitate and residue, see § 89.

The results are more accurate than those obtained by method *a*, since, on the one hand, the bichloride of platinum and chloride of potassium is more insoluble in spirit of wine than the corresponding ammonium salt; and, on the other hand, loss of substance is less likely to arise during the process of ignition than is the case in method *a*. The results would be less accurate were the ignition effected simply in a crucible, instead of in a current of hydrogen gas, since in that case complete decomposition will not ensue, at all events not if the amount of substance acted upon is at all considerable. To weigh the bichloride of platinum and chloride of potassium in that form would not be practicable, as it is impossible to remove, by washing with spirit of wine, all traces of the chloride of potassium thrown down along with it, without, at the same time, dissolving a portion of the double chloride.

c. By Precipitation as Bisulphide of Platinum.

Precipitate the warm solution with sulphuretted hydrogen water or gas, according to its greater or less dilution, heat the mixture to incipient ebullition, filter, wash the precipitate, dry, and ignite (§ 52). For the properties of the precipitate and residue, see § 89. The results are accurate.

d. By Ignition.

Heat in a covered porcelain or platinum crucible, very gently at first, but finally to redness, and weigh the residuary pure platinum. For the properties of the residue, see § 89. The results are most accurate.

e. By Precipitation with reducing Agents.

Various reducing agents may be employed to precipitate platinum from its solutions in the metallic state. The reduction is very promptly effected by pure zinc, the excess of which is removed by hydrochloric acid, somewhat more slowly, and only with application of heat, by alkaline formates. Nitrate of suboxide of mercury also precipitates the whole of the platinum from solution of the bichloride; upon igniting the brown precipitate obtained, fumes of subchloride of mercury escape, and metallic platinum remains.

§ 125.

3. TEROXIDE OF ANTIMONY.

a. Solution.

Teroxide of antimony, and the compounds of that metal which are insoluble in water, or are decomposed by that agent, are dissolved in more or less concentrated hydrochloric acid. Metallic antimony is dissolved best in nitrohydrochloric acid. The ebullition of a hydrochloric acid solution of terchloride of antimony is attended with partial volatilization of the latter; the concentration of a solution of the kind by evaporation involves accordingly loss of substance. Solutions so highly dilute as to necessitate a recourse to evaporation, must therefore previously be supersaturated with potassa. Hydrochloric acid solutions of teroxide of antimony which it is intended to dilute with water, must previously be mixed with tartaric acid, to prevent the separation of basic salt. In diluting hydrochloric acid solution of antimonic acid, the water must not be added gradually and in small quantities at a time, which would make the fluid turbid, but in sufficient quantity at once, which will leave the fluid clear.

b. Determination.

Antimony is weighed either as *tersulphide*, or as *metallic antimony*, or as *antimonious acid* (SbO_4); or it is estimated by volumetrical analysis.

We may convert into

1. TERSULPHIDE OF ANTIMONY.	2. METALLIC ANTIMONY.
All compounds of antimony without exception.	All compounds of antimony without exception.

3. ANTIMONIOUS ACID.

The oxides of antimony, and their salts with readily volatile or decomposable oxygen acids.

Method 1 is most frequently employed, 3 is resorted to only on rare occasions; 2, which may be effected both in the dry and in the humid way, is hardly ever had recourse to except in technical investigations, and to effect the separation of antimony from other bodies. The volumetrical method is only admissible in cases where the antimony is in solution in form of pure teroxide, and can accordingly find but limited application.

1. *Precipitation as Tersulphide of Antimony.*

Add to the antimony solution hydrochloric acid, if not already present, then tartaric acid, and dilute with water, if necessary. Introduce the clear fluid into a flask, closed with a double perforated cork, or with a double perforated india-rubber cap; through one of the perforations passes a tube, bent outside at a right angle, which nearly extends to the bottom of the flask; through the other perforation passes another tube, bent outside twice at right angles, which reaches only a short way into the flask; the outer end of this tube dips slightly under water. Conduct through the first tube sulphuretted hydrogen gas, until it predominates strongly; put the flask in a moderately warm place, and conduct carbonic acid, instead of sulphuretted hydrogen, into the fluid, until the excess of the latter gas is almost completely removed; filter now without intermission through a weighed filter, wash the precipitate rapidly and thoroughly with water mixed with a few drops of sulphuretted hydrogen water, dry at 212° F., and weigh. The precipitate so weighed always retains some water, and may, besides, contain free sulphur, and also—in cases where the antimony solution, besides teroxide or terchloride, contains antimonic acid or pentachloride of antimony—pentasulphide of antimony together with tersulphide. A further examination of the precipitate is accordingly indispensable.

To this end, treat a sample of the weighed precipitate with strong hydrochloric acid. If

a. The sample dissolves to a clear fluid, this is a proof that the precipitate only contains $Sb\,S_3$; but if

b. Sulphur separates, this shows that either a higher sulphide or an admixture of free sulphur is present.

In case *a*, the greater portion of the dried precipitate is weighed in a porcelain boat, which is then inserted into a sufficiently wide glass tube, about 2 decimetres long; a slow current of carbonic acid is transmitted through the latter, and the boat cautiously heated by means of a lamp, moved to and fro under it, until the orange precipitate becomes black; this operation serves to expel the whole of the water present. The precipitate is then allowed to cool, in a current of carbonic acid, and, when cold, weighed; from the amount found, the total quantity of anhydrous sulphide of antimony contained in the entire precipitate is ascertained by a simple calculation. The results are accurate. Experiment No. 76 gave 99·77 instead of 100. But if the precipitate is simply dried at 212° F., the results are about 2·5 per cent. too high—see the same experiment (No. 76). For the properties of the precipitate, see § 90.

In case *b*, the precipitate is subjected to the same treatment as in *a*, with this difference only, that the contents of the boat are heated much more intensely, and the process is continued until no more sulphur is expelled. This removes not only the sulphur combined with $Sb\,S_3$ to $Sb\,S_5$, but also the mechanically admixed sulphur; the residue consists of pure tersulphide of antimony ($Sb\,S_3$). The latter may, by way of control, be dissolved in fuming hydrochloric acid, and the solution precipitated again with sulphuretted hydrogen; the precipitate obtained by this process is sure to be free from any excess of sulphur, and to consist simply of $Sb\,S_3$.

The method described in § 148, of estimating the sulphur in the precipitate dried at 212° F., and calculating the antimony from the difference, does not give accurate results, since the precipitate, besides antimony and sulphur, contains also water. In cases, therefore, where this indirect method is resorted to, this water must first be expelled, as directed in *a*.

The antimony may also be determined in the direct way, in the precipitate dried at 212° F. To this end, an aliquot part of it is weighed in a bulb tube, hydrogen gas transmitted through the latter, and a very gentle heat applied, which is gradually increased, until no more sulphuretted hydrogen escapes. It is hardly possible, however, to avoid a slight loss of antimony in this process, as a small portion of that body is but too apt to be carried away by the hydrogen gas.

2. *Determination as Antimonious Acid.*

Evaporate the compound under examination cautiously with nitric acid, and ignite the residue, until the weight remains constant. The experiment may safely be made in a platinum crucible. In the case of antimonic acid, the evaporation with nitric acid may be omitted. For properties of the residue, see § 90, where I have already pointed out the reason why it is indispensable to ascertain whether the compound produced by the oxidation of the antimony consists, after ignition, really of $Sb\,O_4$.

3. *Volumetrical Analysis.*

The methods proposed to effect the volumetrical estimation of antimony are based, either,

a. Upon the conversion of teroxide of antimony in an alkaline solution into antimonic acid, by means of a standard solution of iodine ($Sb\,O_3 + 2\,I + 2\,Na\,O = Sb\,O_5 + 2\,Na\,I$). *Fr. Mohr*, "Lehrbuch der Titrirmethode," supplement to part I., 371.

b. Upon the conversion of teroxide of antimony in hydrochloric acid solution into antimonic acid, by means of a standard solution of chromate of potassa, and estimation of the excess of the latter, by means of a standard solution of protochloride of iron (*F. Kessler*, "Poggend. Annal.," 95, 204).

c. Upon the conversion of antimony into antimonic acid, reduction of the latter to teroxide, by a standard solution of protochloride of tin, at 104° F., and estimation of the excess of protochloride of tin, by a standard solution of chromate of potassa, after previous addition of some solution of iodide of potassium and starch paste (*A. Streng*, "Pogg. Annal.," 94, 493).

Neither the second nor the third of these methods is calculated to give accurate results. With respect to the second, I have to remark that it is the more difficult to peroxidize the teroxide of antimony in acid solution, by bichromate of potassa or by solution of permanganate of potassa, the more concentrated and acid the solution, different quantities of the oxidizing agents being needed to attain the required point of excess in solutions of different degrees of concentration (comp. experiment No. 77). The third method is altogether unfit for the intended purpose, as estimations made with protochloride of tin and bichromate of potassa are, in themselves, not over reliable. See supplement to §§ 112 and 113, *b.*

And even the first method gives accurate results only under certain very definite conditions; for teroxide of antimony has not invariably the same tendency, in alkaline solution, to change to antimonic acid; but this tendency is greater in presence of a large proportion of alkaline carbonate, than in presence of a small proportion, and becomes constant only in presence of a certain excess of alkaline carbonate. To obtain accurate results, therefore, it is necessary to proceed as follows:

Dissolve a portion of the compound under examination, containing about 0·1 grm. of teroxide of antimony, in about 10 cub. centimet. of tartaric acid and water, and add solution of carbonate of potassa in sufficient quantity to make the fluid about neutral. Add now 20 cub. centimet. of a cold saturated solution of bicarbonate of soda; the fluid will remain clear; add some starch paste, and finally, drop by drop, standard solution of iodine (§ 146), until the fluid, after being stirred, remains just blue, or bluish red. The disappearance of the color, a short time after, must not induce the operator to add any more solution of iodine; 2 equiv. of the iodine used correspond to 1 equiv. of teroxide of antimony.

The results obtained are quite satisfactory (Experiment No. 78). I cannot recommend the use of the simple carbonate of soda, which *Fr. Mohr* employed in his experiments, as that salt has of itself the property of fixing a considerable proportion of iodine, which varies, moreover, with the respective quantity of water used (Exper. No. 79), whilst this is not the case with the bicarbonate (Exper. No. 80). Comp. also § 127, 5, 1, and Exper. No. 81.

§ 126.

4. Protoxide of Tin, and 5. Binoxide of Tin.

a. Solution.

In dissolving compounds of tin soluble in water, a little hydrochloric acid is added to ensure a clear solution. Nearly all the compounds of tin insoluble in water dissolve in hydrochloric acid or in nitrohydrochloric acid. The hydrate of metastannic acid may be dissolved by boiling with hydrochloric acid, decanting the fluid, and treating the residue with a large proportion of water. Ignited binoxide of tin, and compounds of the binoxide insoluble in acids, are prepared for solution in hydrochloric acid, by reducing them to the state of a fine powder, and fusing in a crucible with hydrate of potassa, or soda, in excess. Metallic tin is dissolved best in nitrohydrochloric acid; it is generally determined, however, by converting it into binoxide, without previous solution. Acid solutions of tin, which contain hydrochloric acid, or a chloride, cannot be concentrated by evaporation, not even after addition of nitric acid or sulphuric acid, without volatilization of bichloride of tin taking place.

b. Determination.

Tin is weighed in the form of *binoxide*, into which it is converted, either by the agency of nitric acid, or by precipitation as hydrated binoxide, or by precipitation as sulphide.

Although a great many volumetrical methods of estimating tin have been proposed, there is not one of them that answers the requirements of science. Even the best of the volumetrical methods in use—viz., the conversion of the protochloride of tin into bichloride, by means of a standard solution of iodine, the completion of the reaction being marked by the blue coloration of the fluid, upon addition of starch paste—gives somewhat reliable results, only if the quantity of tin is not calculated after the formula, $Sn\,Cl + H\,Cl + I = Sn\,Cl_2 + I\,H$, but from an empirical formula obtained by making the iodine solution act first upon the solution of a known quantity of tin dissolved to protochloride,* and then upon the solution in which the amount of protochloride present is to be estimated. The quantity of iodine solution used in the first experiment is to the known quantity of tin, as the quantity of iodine solution consumed in the second experiment is to the unknown quantity. Compare *Fr. Mohr's* experiments, "Lehrbuch der Titrirmethode," page 308.

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* To procure a solution of protochloride of tin of known strength, a weighed quantity of pure tin filings is boiled with hydrochloric acid, with addition of platinum shreds, until dissolved; or a weighed quantity of protochloride of tin and chloride of ammonium ($Sn\,Cl + N\,H_4\,Cl + aq.$) is boiled in water containing hydrochloric acid.

$SnO_2 + HNO_3 =$

We may convert into

BINOXIDE OF TIN.

a. By the agency of Nitric Acid.

Metallic tin, and those compounds of tin which contain no fixed acid, provided no compounds of chlorine be present.

b. By Precipitation as Hydrated Binoxide.

All compounds of tin containing volatile acids, provided no non-volatile organic substances nor sesquioxide of iron be present.

c. By Precipitation as Sulphide.

All compounds of tin without exception.

In methods *a* and *c*, it is quite indifferent whether the tin is present in the state of protoxide or in that of binoxide. The method *b* requires the tin to be present in the state of binoxide; for the methods of determining the protoxide and binoxide in presence of each other, I refer to Section V.

1. *Determination of Tin as Binoxide.*

a. By Treating with Nitric Acid.

This method is resorted to principally to convert the metallic tin into binoxide. For this purpose the finely-divided metal is put into a capacious flask, and moderately concentrated pure nitric acid (about 1·3 sp. gr.) gradually poured over it; the flask is then covered with a watch glass. When the first tumultuous action of the acid has somewhat abated, a gentle heat is applied until the binoxide formed appears of a pure white color, and further action of the acid is no longer perceptible. Water is then added, and the fluid filtered off; the binoxide is washed, dried, ignited, and weighed. The ignition is effected best in a small porcelain crucible, according to the directions given in § 53; still a platinum crucible may also be used. Compounds of tin which contain no fixed substances may be converted into binoxide by treating them in a porcelain crucible with nitric acid, evaporating to dryness, and igniting the residue. If sulphuric acid be present, the expulsion of that acid may be promoted, in the last stages of the process, by carbonate of ammonia, as in the case of bisulphate of potassa (§ 97). For the properties of the residue, see § 91. The results are accurate.

b. By Precipitation as Hydrate of Binoxide.

The application of this method presupposes the whole of the tin to be present in the state of binoxide or bichloride. Therefore, if a solution contains protoxide, this must first be converted into binoxide, before the quantitative estimation can be proceeded with. For this purpose, mix the solution with chlorine water, conduct chlorine gas into it, or heat gently with chlorate of potassa, until the conversion of the protoxide into binoxide is effected. When this has been done, add ammonia until a permanent precipitate just begins to form, and then hydrochloric acid, drop by drop, until this precipitate is completely redissolved; by this means a large excess of hydrochloric acid in the solution will be avoided. Add to the fluid so prepared a concentrated solution of sulphate of soda (or nitrate of potassa, or nitrate of soda, or nitrate of ammonia), and apply heat, whereupon the whole of the tin will precipitate as hydrate of binoxide. Decant three times on to a filter, then collect the precipitate on the latter, wash thoroughly, dry, and ignite. To make quite sure that the whole of the tin has separated, you need simply;

before proceeding to filter, add a few drops of the clear supernatant fluid to a hot solution of sulphate of soda, when the formation or non-formation of a precipitate will at once decide the question.

This method, which we owe to *J. Löwenthal*, who has also repeatedly tested its merits in my own laboratory ("Journ. für prakt. Chem.," 56, 366), is easy and convenient, and gives very accurate results. The decomposition is expressed by the equation $\mathrm{Sn\,Cl_2 + 4\,Na\,O, S\,O_3 + 4\,H\,O = Sn\,O_2, 2\,H\,O + 2\,Na\,Cl + 2\,(Na\,O, H\,O, 2\,S\,O_3)}$.

c. By Precipitation as Protosulphide or Bisulphide of Tin.

Precipitate the dilute neutral or acid solution with sulphuretted hydrogen water or gas. If the tin was present in the solution in the form of protoxide, and the precipitate consists accordingly of the brown protosulphide, keep the solution, supersaturated with sulphuretted hydrogen, standing for half an hour in a moderately warm place, and then filter; if, on the other hand, the solution contain a salt of binoxide of tin, and the precipitate consists accordingly of the yellow bisulphide, put the fluid, loosely covered, in a warm place, until the odor of sulphuretted hydrogen has nearly gone off, and then filter. Put the filter, with the not yet quite dry precipitate on it, into a porcelain crucible, and apply a very gentle heat, with free access of air, until the odor of sulphurous acid is no longer perceptible. Increase the heat now gradually to a high degree of intensity, and treat the residue repeatedly with some carbonate of ammonia (see *a*), in order to insure the complete expulsion of the sulphuric acid which may be present. Were you to apply a very intense heat from the beginning, fumes of bisulphide of tin would escape, which would be converted into binoxide (*H. Rose*). For the properties of the precipitates, see § 91. The results are accurate.

§ 127.

6. Arsenious Acid, and 7. Arsenic Acid.

a. Solution.

The compounds of arsenious and arsenic acids which are not soluble in water are dissolved in hydrochloric acid or in nitrohydrochloric acid. Some native arsenates of metallic oxides require fluxing with carbonate of soda, as an indispensable preliminary to their solution. Metallic arsenic and metallic arsenides are dissolved in nitrohydrochloric acid; those metallic arsenides which are insoluble in this menstruum are fused with carbonate of soda and nitrate of potassa, by which means they are converted into soluble arsenates of the alkalies and insoluble metallic oxides. All solutions of compounds of arsenic which have been effected by heating with nitrohydrochloric acid, or chlorine in excess, contain arsenic acid. A solution of arsenious acid in hydrochloric acid cannot be concentrated by boiling, since chloride of arsenic would escape with the hydrochloric acid fumes. This, however, is much less likely to take place if the solution contains arsenic acid; it is advisable in all cases where a hydrochloric acid solution containing arsenic is to be concentrated, to render the same previously alkaline.

b. Determination.

Arsenic is weighed *as arsenate of lead*, or as *arsenate of magnesia and ammonia*, or as *arsenate of sesquioxide of iron*, or as *tersulphide of arsenic*; it may be estimated also in an *indirect* way, and by *volumetrical analysis*.

We may convert into

1. ARSENATE OF LEAD.

Arsenious and arsenic acids in aqueous or nitric acid solution. (Acids or salt-radicals forming fixed salts with oxide of lead or metallic lead, must not be present.)

2. ARSENATE OF MAGNESIA AND AMMONIA.

a. By direct Precipitation.

Arsenic acid in all solutions free from bases or acids precipitable by magnesia or ammonia.

b. Preceded by Precipitation as Arsenio-Molybdate of Ammonia.

Arsenic acid in all cases where no phosphoric acid is present, nor any substance by which molybdic acid is decomposed.

3. ARSENATE OF SESQUIOXIDE OF IRON.

Arsenic acid in solutions free from such substances precipitable by sesquichloride of iron with addition of ammonia or carbonate of baryta.

4. TERSULPHIDE OF ARSENIC.

All compounds of arsenic without exception.

The volumetrical methods are very practical and convenient, in all cases where the arsenic is present as arsenious acid or as an alkaline arsenate; they have now almost entirely superseded the indirect gravimetrical methods formerly employed to effect the quatitative estimation of arsenious acid.

1. *Determination as Arsenate of Lead.*

a. Arsenic Acid in Aqueous Solution.

A weighed portion of the solution is put into a platinum or porcelain dish, and a weighed amount of recently ignited pure oxide of lead added (about five or six times the supposed quantity of arsenic acid present); the mixture is cautiously evaporated to dryness, and the residue heated to gentle redness. and maintained some time at this temperature. The residue is arsenate of lead + oxide of lead. The quantity of arsenic acid is now readily found by subtracting from the weight of the residue that of the oxide of lead added.

For the properties of arsenate of lead, see § 92. The results are perfectly accurate, provided the residue be not heated beyond gentle redness.

b. Arsenious Acid in Solution.

Mix the solution with nitric acid, add a weighed quantity of oxide of lead in excess, evaporate to dryness, and ignite the residue most cautiously in a covered crucible, until the whole of the nitrate of lead is decomposed. The residue consists here also of arsenic acid + oxide of lead. This method requires considerable care to guard against loss by decrepitation upon ignition of the nitrate of lead.

2. *Estimation as Arsenate of Magnesia and Ammonia.*

a. By Direct Precipitation.

This method, which was first recommended by *Levol*, presupposes that the whole of the arsenic is contained in the solution in the form of arsenic acid. Where this is not the case, the solution is gently heated, in a capacious flask, with hydrochloric acid, and chlorate of potassa added in small portions, until the fluid emits a strong smell of chlorous acid; it is then allowed to stand at a gentle heat until the odor of this gas is nearly gone off.

The arsenic acid solution is now mixed with ammonia in excess, which must not produce turbidity, even after standing some time; a solution of sulphate of magnesia is then added, containing chloride of ammonium in sufficient quantity to prevent the fluid being rendered turbid by ammonia. (The best way is to keep a solution of sulphate of magnesia mixed with chloride of ammonium and ammonia ready prepared in the laboratory—see § 62, 7.) The fluid, which smells strongly of ammonia, is allowed to stand 12 hours in the cold, and then filtered through a weighed filter; the precipitate on the filter is washed with a mixture of 3 parts of water and 1 part of solution of ammonia, dried at 212° F., and weighed. It has the formula $As O_5, 2 Mg O, N H_4 O + aq.$ For the properties of the precipitate, see § 92. This method gives very satisfactory results ("Journal f. prakt. Chem.," 56, 32).

b. Preceded by Precipitation as Arsenio-molybdate of Ammonia.

Add to a solution of molybdate of ammonia nitric acid until the precipitate which forms at first is redissolved. Mix the solution so prepared with the acid solution under examination, which must be free from phosphoric acid and silicic acid, and proceed exactly in the same way as with phosphoric acid—see § 134, *b*, *β*. Treat the arsenate of magnesia and ammonia thrown down from the ammoniacal solution of the arsenio-molybdate of ammonia by a mixture of sulphate of magnesia, chloride of ammonium, and ammonia, as in *a*. Results satisfactory.

3. *Estimation as Arsenate of Sesquioxide of Iron.*

(*Berthier* and *V. Kobell's* method).

a. The Solution contains no other fixed Bases besides Alkalies.

Add to the solution a measured quantity of solution of sesquioxide of iron of known strength, and precipitate with ammonia. The precipitate must be reddish brown: if not of that color, it is a sign that a sufficient quantity of the solution of sesquioxide of iron has not been added. Let the precipitated liquid stand some time at a gentle heat; filter, wash, and dry the precipitate; expose the dry precipitate first to a very gentle heat, to ensure the expulsion of the ammonia at a temperature at which it cannot exercise a reducing action upon the arsenic acid; after a time, increase the heat gradually, at last to intense ignition; keep the residue in this state until the weight remains constant. The residue is basic arsenate of sesquioxide of iron + sesquioxide of iron, or, differently expressed, sesquioxide of iron + arsenic acid. Deduct from the weight of the residue the weight of the sesquioxide of iron added: the difference expresses the quantity of arsenic acid contained in the analysed solution. A solution of sesquioxide of iron of known strength may be prepared either by dissolving a weighed quantity of fine pianoforte wire in nitric acid (100 of wire being assumed to give 142·4 of sesquioxide), or by precipitating a nitric acid solution of sesquioxide of iron of unknown strength with ammonia, washing, drying, and igniting (§ 113, 1, *a*). The results are satisfactory ("Journal f. prakt. Chem.," 56, 32).

b. The Solution contains other fixed Bases besides Alkalies.

The preceding method of *Berthier* is modified as follows, provided the bases present in the solution are not precipitated by carbonate of baryta in the cold. The solution is mixed with solution of sesquioxide of iron of known strength, as in *a*, but instead of ammonia, carbonate of baryta is added in excess (should the fluid contain a large excess of free acid, it is advisable to nearly neutralize this previously with carbonate of soda; the fluid must, however, still remain clear). The mixture is then allowed to stand several hours in the cold, and the precipitate, which contains the whole of the sesquioxide of iron, the whole of the arsenic acid, and some carbonate of baryta, is washed with cold water, first by decantation, then upon the filter, dried, gently ignited for some time, and weighed. The residue is dissolved in hydrochloric acid, the amount of baryta contained in it determined by means of sulphuric acid, the sulphate of baryta obtained calculated upon carbonate, and the calculated weight, together with the known weight of the sesquioxide of iron, subtracted from the weight of the original residue: the difference expresses the quantity of arsenic acid contained in the analysed solution. This method, which is recommended by *Kobell*, presupposes the absence of sulphuric acid. In cases, therefore, where that acid is present, it must be removed before the carbonate of baryta can be added; which is effected by precipitating with chloride of barium, and filtering off the precipitate.

4. *Determination as Tersulphide of Arsenic.*

a. In Solutions of Arsenious Acid or Arsenites, free from Arsenic Acid.

Precipitate with sulphuretted hydrogen, and expel the excess of the precipitant by carbonic acid, conducting the process in the same way as with antimony—see § 125, 1. Wash the precipitated tersulphide of arsenic, dry at 212° F., and weigh. Particles of the precipitate adhering so firmly to the glass tube that mechanical means fail to remove them are dissolved in ammonia, and then precipitated again by hydrochloric acid. For the properties of the precipitate, see § 92. The results are accurate.

If the solution contains a substance which decomposes sulphuretted hydrogen, such as sesquioxide of iron, chromic acid, &c., the free sulphur which precipitates with the tersulphide of arsenic, destroys the accuracy of the results. In such cases the precipitate is dissolved in solution of potassa, and chlorine transmitted through the solution (§ 148, II. 2, *b*). In the solution produced, which contains the sulphur as sulphuric acid, the arsenic as arsenic acid, the latter is determined as in 2, *a*; or the sulphuric acid is estimated, the quantity found calculated upon sulphur, and the calculated weight of the latter subtracted from that of the mixed precipitate of tersulphide of arsenic and sulphur. Another method, which has been recommended, viz., to treat the mixed precipitate with ammonia, which is said to dissolve the tersulphide of arsenic, leaving the sulphur undissolved, gives only approximate results, as some of the sulphur dissolves in the ammoniacal solution of the tersulphide of arsenic.

b. In Solutions of Arsenic Acid or Arsenates, or of a mixture of the two Oxides of Arsenic.

Mix the solution, in a flask, with a strong aqueous solution of sulphurous acid in excess, place the flask in a slanting position, and heat slowly to near ebullition; keep the mixture at a temperature below the boiling point, until the fluid smells no longer of sulphurous acid, and treat the solution, which now contains only arsenious acid, as in *a*. Great care is required in this process to guard against loss from the formation and escape of chloride of arsenic.

5. *Volumetrical Methods.*

a. Fr. Mohr's method ("Lehrbuch der Titrirmethode," page 295). The method is based upon the same principle as the one given for teroxide of antimony, in § 125, 3, *a*, *i.e.* conversion of arsenious acid in alkaline solution into arsenic acid by solution of iodine ($As\,O_3 + 2\,Na\,O + 2\,I = As\,O_5 + 2\,Na\,I$).

If, therefore, you have arsenious acid or an alkaline arsenite in aqueous solution, mix a weighed or measured quantity of the fluid, containing about 0·1 grm. $As\,O_3$, with 20 cubic centimetres of a saturated solution of bicarbonate of soda, purified by washing with water; add some starch paste, then standard solution of iodine (§ 146), until the iodide of starch reaction just makes its appearance; reckon for every 2 eq. of iodide used 1 eq. of arsenious acid. If the solution of arsenious acid is acid, you must first neutralize it with pure carbonate of soda, if alkaline, with pure hydrochloric acid, before proceeding to add the bicarbonate of soda. Of course, the solution must contain no substances exercising a decomposing action upon solution of iodine ($S\,O_2$, $S_2\,O_2$). The results are accurate. Comp. experim. No. 81, from which it will be seen that the carbonate of soda may be used instead of the bicarbonate. The reason why the excess of the salt is, under these circumstances, less unfavorable to the accuracy of the results, than when iodine is made to act upon a pure aqueous solution of it, as in experiment No. 79, is attributable simply to the fact that it is the neutral compound alone which acts upon iodine; but not a compound containing more carbonic acid than the neutral salt. Now, in my experiments, the salt was converted into the latter state, because, in the first place, the solution of the arsenious acid was slightly acid, and, in the second place, upon the conversion of the arsenious into arsenic acid, more soda is fixed, and carbonic acid accordingly liberated. However, the use of the bicarbonate is still to be preferred as the safer way.

b. Bunsen's method ("Annal. d. Chem. u. Pharm.," 86, 209).

This ingenious method is based upon the following facts :—

aa. If bichromate of potassa is boiled with concentrated hydrochloric acid, 3 equivalents of chlorine are disengaged to every 2 equivalents of chromic acid ($2\,Cr\,O_3 + 6\,H\,Cl = Cr_2Cl_3 + 3\,Cl + 6\,H\,O$).

bb. But if arsenious acid is present (not in excess) there is not the quantity of chlorine disengaged corresponding to the chromic acid, but so much less of that element, as is required to convert the arsenious into arsenic acid ($As\,O_3 + 2\,Cl + 2\,H\,O = As\,O_5 + 2\,H\,Cl$). Consequently, for every 2 equivalents of chlorine obtained less in proportion to the chromic acid is to be reckoned 1 equivalent of arsenious acid.

cc. The quantity of the chlorine is estimated by determining the quantity of iodine liberated by it from iodide of potassium.

These are the principles of *Bunsen's* method. For the manner of execution, I refer to § 130, I. *d*, *β*.

The method recommended by *Kessler* ("Pogg. Annal.," 95, 204) is analogous to that given in § 125, 3, *b*, for the volumetrical estimation of teroxide of antimony, and is, for the reason there stated, unsuited for the purpose. The same remark applies to *P. Kotschoubey's** adaptation of *Räwsky's* method of determining phosphoric acid.

6. *Estimation of Arsenious Acid by indirect Gravimetrical Analysis.*

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* "Journ. f. prakt. Chem.," 49, 185.

a. Rose's method. Add to the hydrochloric acid solution, in the preparation of which care must be taken to exclude oxidizing substances, sodio- or ammonio-terchloride of gold in excess, and digest the mixture for several days, in the cold, or, in the case of dilute solutions, at a gentle warmth; then weigh the separated gold as directed in § 123. Keep the filtrate to make quite sure that no more gold will separate. 2 eq. of gold correspond to 3 eq. of arsenious acid.

b. Vohl's ("Annal. d. Chem. u. Pharm.," 94, 219) method. Mix the solution under examination with a weighed quantity of bichromate of potassa, and free sulphuric acid; estimate the chromic acid still present by the method given in § 130, *c*, and deduce from the quantity of that acid consumed in the process, *i. e.*, reduced by the arsenious acid, the quantity of the latter, after the formula $3\ As\ O_3 + 4\ Cr\ O_3 = 3\ As\ O_5 + 2\ Cr_2\ O_3$.

Supplement to the Sixth Group.

§ 128.

8. MOLYBDIC ACID.

Molybdic acid is converted, for the purpose of its quantitative estimation either into binoxide of molybdenum, or into molybdate of lead, or into bisulphide of molybdenum.

a. Pure molybdic acid ($Mo\ O_3$), and also molybdate of ammonia, may be reduced to binoxide ($Mo\ O_2$), by heating in a current of hydrogen gas. The best way of effecting this is to introduce the molybdic acid, or molybdate of ammonia, into a small porcelain boat, insert this into a wider glass tube, and heat until the weight remains constant. The heat must not be carried beyond gentle redness.

b. The following is the best method of precipitating molybdic acid from an alkaline solution. Dilute the solution, if necessary, neutralize the free alkali with nitric acid, and allow the carbonic acid, which may be liberated in the process, to escape, then add solution of neutral nitrate of suboxide of mercury. The yellow precipitate formed appears at first bulky, but after several hours' standing it shrinks; it is insoluble in the fluid, which contains an excess of nitrate of suboxide of mercury. Collect the precipitate on a filter, and wash with a dilute solution of nitrate of suboxide of mercury, as it is slightly soluble in pure water. Dry, remove the dry precipitate as completely as practicable from the filter, and determine the molybdenum in it as directed in *a* (*H. Rose*); or mix the precipitate, together with the filter ash, with a weighed quantity of ignited oxide of lead, and ignite until all the mercury is expelled; then add some nitrate of ammonia, ignite again and weigh. The excess obtained over and above the weight of the oxide of lead used, is molybdic acid (*Seligsohn*), "Journ. f. prakt. Chem.," 67, 472.

c. The precipitation of molybdenum as sulphide is always a difficult operation. If the acid solution is supersaturated with sulphuretted hydrogen, warmed, and filtered, the filtrate and washings are generally still colored. They must, accordingly, be warmed, and sulphuretted hydrogen again added, and the operation must afterwards, if necessary, be repeated until the washings appear almost colorless. The precipitation succeeds better when the sulphide of molybdenum is dissolved in a relatively large excess of sulphide of ammonium, and, after the fluid has acquired a reddish-yellow tint, precipitated with hydrochloric acid. *Zenker* ("Journ. f. prakt. Chem.," 58, 259) advises to boil, after precipitation, until the sulphuretted hydrogen is expelled, and then to wash with hot water, taking care to slightly acidify the first portion of the water used in the washing process. The brown sulphide of molybdenum is collected on a weighed filter, and the molybdenum determined is an aliquot part of it, by gentle ignition in a current of hydrogen gas, as in *a*. The brown sulphide of molybdenum changes in this process to the gray bisulphide ($Mo\,S_2$) [*H. Rose*].

II. QUANTITATIVE DETERMINATION OF THE ACIDS IN COMPOUNDS CONTAINING ONLY ONE ACID, FREE OR COMBINED;—AND SEPARATION OF THE ACIDS FROM THE BASES.

FIRST GROUP.

First Division.

Arsenious Acid—Arsenic Acid—Chromic Acid—(Selenious Acid, Sulphurous and Hyposulphurous Acids, Iodic Acid).

§ 129.

1. Arsenious and Arsenic Acids.

For the quantitative estimation of these two acids, I refer to § 127; the methods of separating them from the bases will be found in Section V.

§ 130.

2. Chromic Acid.

I. Determination.

Chromic acid is determined either in the form of *sesquioxide of chromium*, or in that of *chromate of lead*. But it may be estimated also from the quantity of carbonic acid disengaged by its action upon oxalic acid in excess, and also by volumetrical analysis. In employing the first method, it must be borne in mind that 1 equiv. of sesquioxide of chromium ($Cr_2\,O_3$) corresponds to 2 equiv. of chromic acid 2 ($Cr\,O_3$).

a. Determination as Sesquioxide of Chromium.

α. The chromic acid is reduced to the state of sesquioxide, and the amount of the latter determined (§ 106). The reduction is effected, either by heating the solution with hydrochloric acid and alcohol; or by mixing hydrochloric acid with the solution, and conducting sulphuretted hydrogen into the mixture; or by adding a strong solution of sulphurous acid, and applying a gentle heat. With concentrated solutions the first method is generally resorted to, with dilute solutions one of the two latter. With respect to the first method, I have to remark that the alcohol must be expelled before the sesquioxide of chromium can be precipitated with ammonia; and with respect to the second, that the solution supersaturated with sulphuretted hydrogen must be allowed to stand in a moderately warm place, until the separated sulphur has completely subsided. The results are accurate.

β. The neutral or slightly acid (nitric acid) solution, is precipitated with nitrate of suboxide of mercury, the red precipitate of chromate of suboxide of mercury filtered off, washed with a dilute solution of nitrate of suboxide of mercury, dried, ignited, and the residuary sesquioxide of chromium weighed (*H. Rose*).

b. *Determination as Chromate of Oxide of Lead.*

The solution is mixed with acetate of soda in excess, and, if necessary, acetic acid added until the reaction is slightly acid; the solution is then precipitated with neutral acetate of oxide of lead. The washed precipitate is either collected on a weighed filter, dried in the water-bath, and weighed; or it is gently ignited as directed § 53, and then weighed. For the properties of the precipitate, see § 93. The results are accurate.

c. *Determination by means of Oxalic Acid* (*Vohl's* method).

When chromic acid and oxalic acid are brought together, the former yields oxygen to the latter: sesquioxide of chromium is formed, and carbonic acid escapes ($2\,Cr\,O_3 + 3\,C_2\,O_3 = Cr_2\,O_3 + 6\,C\,O_2$). Three equivalents of carbonic acid (66) correspond accordingly to one equivalent of chromic acid (50·78). The *modus operandi* is the same as that which will be given hereafter in the chapter on the examination of manganese ores (§ 230). 1 part of chromic acid requires 2¼ parts of oxalate of soda. If it is intended to determine in the residue the alkali which was combined with the chromic acid, oxalate of ammonia is used.

d. *Determination by Volumetrical Analysis.*

α. *Schwarz's* method.

The principle of this method is identical with that upon which *Penny's* method of determining iron is based (§ 112, 2, *b*). The execution is simple: acidify the not too dilute solution of the chromate with sulphuric acid, add a measured excess of solution of protoxide of iron, the strength of which you have previously ascertained according to the directions of § 112, 2, *a*, or *b*, or the solution of a weighed quantity of sulphate of protoxide of iron and ammonia, and then determine in the manner directed § 112, 2, *a*, or *b*, the quantity of protoxide of iron remaining. The difference shows the amount of iron that has been converted by the chromic acid from the state of protoxide to that of sesquioxide. 1 gramme of iron corresponds to 0·6045 of chromic acid. To determine the chromic acid in chromate of lead, the latter is, after addition of the sulphate of protoxide of iron and ammonia, most thoroughly triturated with hydrochloric acid, water added, and the analysis then proceeded with as directed § 112, 2, *a*, or *b*.

β. *Bunsen's* method ("Ann. der Chem. u. Pharm.," 86, 279).

If a chromate is boiled with an excess of fuming hydrochloric acid, there are disengaged for every 2 equivalents of chromic acid 3 equivalents of chlorine; for instance, $K\,O, 2\,Cr\,O_3 + 7\,H\,Cl = K\,Cl + Cr_2\,Cl_3 + 7\,H\,O + 3\,Cl$. If the escaping gas is conducted into solution of iodide of potassium in excess, the 3 equivalents of chlorine set free 3 equivalents of iodine. By determining the quantity of the latter element in the manner described in § 146, we find the quantity of the chromic acid; 380·64 of iodine corresponding to 101·56 of chromic acid.

The analytical process is conducted as follows:—put the weighed sample of the chromate into the little flask *d* (Fig. 65), (blown before the lamp, and holding only from 36 to 40 cubic centimetres,) fill the flask to two-thirds with fuming hydrochloric acid, and connect the bulbed evolution tube with the neck of the flask by means of a stout tight-closing vulcanized india-rubber tube *c*. As shown in the engraving, *a* is a pipette, drawn out, at the lower end, into an upturned point. A loss of chlorine need not be apprehended in this operation, as the disengagement of that gas begins only upon the application of heat. Insert the evolution tube into the neck of the retort *a b*, which is filled to two-thirds with solution of iodide of potassium.* This retort holds about 160 c.c. The neck presents two small expansions, blown before the lamp, and intended, the lower one, to receive the liquid which is forced up during the operation, the upper one, to serve as an additional guard against spurting. Apply now, cautiously, heat to the flask containing the chromate. After two or three minutes' ebullition, the whole of the chlorine has passed over, and is replaced by its equivalent of free iodine in the iodide of potassium solution. When the ebullition is at an end, take hold of the caoutchouc tube *c* with the left hand, and, whilst steadily holding the lamp under the flask with the right, lift *a* so far out of the retort that the curved point is in the bulb *b*. Now remove first the lamp, then the flask, dip the retort in cold water, to cool it, and shake the fluid in it about to effect the complete solution of the separated iodine in the excess of iodide of potassium solution. When the fluid is quite cold, transfer it to a beaker, rinsing the retort into the beaker, and proceed as directed § 146. The method gives very satisfactory results. The apparatus here recommended differs slightly from that used by *Bunsen*, the retort of the latter having only one bulbous expansion in the neck, and the evolution tube no bulb, being closed instead, at the lower end, by a glass or caoutchouc valve, which permits the exit of the gas from the tube, but opposes the entrance of the fluid into it. I think the modifications which I have made in *Bunsen's* apparatus, are calculated to facilitate the success of the operation. This method of estimating chromic acid is based simply upon the determination of the quantity of chlorine evolved upon boiling the chromate with strong hydrochloric acid; and it is self-evident, therefore, that *Fr. Mohr's* method, described § 142, may also be employed for the same purpose.

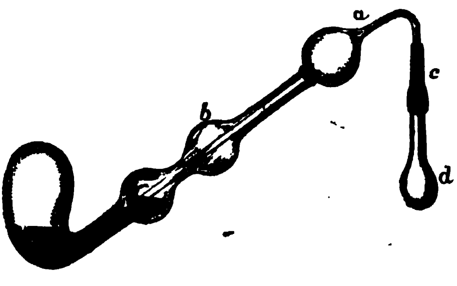

Fig. 65.

II. Separation of Chromic Acid from the Bases.

a. Of the First Group.

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* 1 part of pure iodide of potassium, free from iodic acid, dissolved in 10 parts of water. The fluid must show no brown tint immediately after addition of hydrochloric acid.

α. Reduce the chromic acid as directed in I., and separate the sesquioxide of chromium from the alkalies as directed in § 155.

β. Mix the chromate of potassa or soda with about 2 parts of dry pulverized chloride of ammonium, and heat the mixture cautiously. The residue contains the chloride of the alkalies and sesquioxide of chromium, which may be separated by water.

γ. Chromate of ammonia is reduced to sesquioxide of chromium by cautious ignition.

b. OF THE SECOND GROUP.

a. Fuse the compound under examination with 4 parts of carbonate of soda and potassa, and treat the fused mass with hot water, which dissolves the chromic acid in the form of an alkaline chromate. The residue contains the alkaline earths in the form of carbonates; but as it contains also an admixture of alkali, it cannot be weighed directly. The chromic acid in the solution is determined as in I. Chromate of baryta (and most probably also the chromate of strontia and lime) may, as shown by *H. Rose* ("Journ. f. prakt. Chem.," 66, 166), be readily and completely decomposed also by simple boiling with an excess of solution of potassa or soda.

β. Dissolve in hydrochloric acid, reduce the chromic acid according to the directions of I., *a*, and separate the sesquioxide of chromium from the alkaline earth according to § 156.

γ. Chromate of magnesia as well as other chromates of the alkaline earths soluble in water may be easily decomposed also, by determining the chromic acid according to I., *a*, *β*, or I., *b*, and separating the magnesia, &c., in the filtrate from the excess of the salt of mercury or lead as directed § 162.

δ. Chromates of baryta, strontia, and lime may also be decomposed by the method described II., *a*, *β*. Compare *Bahr*, analysis of bichromate of baryta, lime, &c., "Journ. f. prakt. Chem.," 60, 60.

c. OF THE THIRD GROUP.

α. *From Alumina.*

Precipitate the alumina by ammonia or carbonate of ammonia (§ 105), and determine the chromic acid in the filtrate according to the directions given in I. (compare also § 157.)

β. *From Sesquioxide of Chromium.*

aa. Determine in one portion the quantity of the chromic acid according to I., *c*, or I., *d*, *a*, or *β*, and in another portion the total amount of the chromium, either by cautious ignition with chloride of ammonium, or by conversion into sesquioxide according to I., *a*, or by converting, in the first place, into chromic acid according to § 106, 2.

bb. In many cases the chromic acid may be precipitated according to I., *a*, *β*, or I., *b*. The sesquioxide of chromium and suboxide of mercury, or oxide of lead, in the filtrate as directed § 162.

d. OF THE FOURTH GROUP.

α. Proceed as directed in *b*, *a*. Upon treating the fused mass with hot water, the metals are left as oxides. In the case of manganese the fusion must be effected in a bulb-tube in a stream of carbonic acid gas.

β. Reduce the chromic acid as directed in I., *a*, and separate the sesquioxide of chromium from the metals of the fourth group, as directed in § 160.

e. Of the Fifth and Sixth Groups.

a. Mix the solution with free acid, either at once or after previous reduction of the chromic acid by sulphurous acid, and precipitate with sulphuretted hydrogen. The metals of the fifth and sixth groups precipitate in conjunction with free sulphur (§§ 115 to 127), the chromic acid is reduced. Filter, and determine the sesquioxide of chromium in the filtrate, as directed in I., *a*.

β. Chromate of lead may be decomposed by heating with hydrochloric acid and some alcohol; the chloride of lead and protochloride of chromium formed are subsequently separated by means of alcohol (compare § 162). The alcoholic solution ought always to be tested with sulphuric acid; should a precipitate of sulphate of lead form, this must be filtered off, weighed, and taken into account (compare also § 130, I., *d*).

Supplement to the First Division.

§ 131.

1. Selenious Acid.

From aqueous or hydrochloric acid solutions of selenious acid, the selenium is precipitated by sulphurous acid gas or, in presence of an excess of acid, by sulphite of soda. If the solution contains nitric acid, this must be removed first by evaporation with hydrochloric acid. The precipitated liquid is heated to boiling for ¼ hour, which changes the precipitate from its original red color to black, and makes it dense and heavy. Some more sulphurous acid is now transmitted through the liquid, or sulphite of soda added to it, to see whether any more selenium will separate; the precipitate is finally collected on a weighed filter, dried at a temperature somewhat below 212° F., and weighed. To make quite sure that all the selenium has been removed, the filtrate is evaporated to a small volume, which is then boiled with strong hydrochloric acid, and tested once more with sulphurous acid for selenium. The boiling with hydrochloric acid has for its object to convert the selenic acid which might be present, into selenious acid

As regards the separation of selenious acid from the bases, the following brief directions will suffice:—

a. If the bases are not liable to be altered by the action of sulphurous acid, the latter agent may be used at once to precipitate the selenium.

b. From bases which are not thrown down from acid solution by hydrosulphuric acid, the selenious acid is separated by sulphuretted hydrogen. The moist precipitate of sulphide of selenium is digested with hydrochloric acid and chlorate of potassa until complete solution is effected, or only a small quantity of yellow sulphur left undissolved; the solution is warmed, until all smell of chlorine is gone, and then finally precipitated with sulphurous acid.

c. From the other bases the separation of the selenious acid (and also of selenic acid) is effected by fusing the compound with 2 parts of carbonate of soda and 1 part of nitrate of potassa, extracting the fused mass thoroughly by boiling with water, saturating the filtrate, if necessary, with carbonic acid, to free it from lead which it might contain, then acidifying the fluid with hydrochloric acid, boiling and evaporating (to reduce the selenic acid and drive off the nitric acid), and precipitating finally with sulphurous acid.

Selenium, if pure, must volatilize without residue when heated in a tube.

2. Sulphurous Acid.

To estimate free sulphurous acid in a fluid which may contain also other acids (sulphuric acid, hydrochloric acid, acetic acid), a weighed quantity of the fluid is diluted with water, absolutely free from air,* until the diluted liquid contains only 0·05 per cent. by weight of sulphurous acid; some starch paste is now added, and then solution of iodine of known strength, until the iodide of starch reaction makes its appearance. The reaction which, under these circumstances, takes place is represented by the equation

$$I + HO + SO_2 = IH + SO_3.$$

1 equivalent of iodine added corresponds accordingly to 1 equivalent of sulphurous acid. For the details of the process I refer to § 146. In the case of sulphites soluble in water or acids, water perfectly free from air is poured over the substance under examination, in sufficient quantity to attain the degree of dilution stated above, sulphuric or hydrochloric acid added in excess, and then starch paste and solution of iodine as above. The greatest care must be taken, in this method, to use, for the purpose of dilution, water absolutely free from air.

Sulphurous acid may also be determined in the gravimetrical way, by conversion into sulphuric acid, and precipitation of the latter with baryta, according to the directions of § 132. This method is especially applicable in the case of sulphites quite free from sulphuric acid. The conversion of the sulphurous into sulphuric acid is effected in the humid way, best by saturating the fluid with chlorine, and warming; in the dry way, by heating the salt, in a platinum crucible, with 4 parts of a mixture of carbonate of soda and nitrate of potassa in equal proportions.

3. Hyposulphurous Acid.

Hyposulphurous acid, in form of soluble hyposulphites, may be determined by means of iodine, in a similar way as sulphurous acid. The reaction is represented by the equation

$$2\,(NaO, S_2O_2) + I = NaO, S_4O_5 + NaI.$$

The salt under examination is dissolved in a large amount of water, starch paste added, and then solution of iodine until the blue color make its appearance. That this method can give correct results only in cases where no other substances acting upon iodine are present, need hardly be mentioned. In the case of dilute fluids the results are the same, if the fluid is acidified before adding the solution of iodine, and the operation proceeded with so quickly that no time is left for the free hyposulphurous acid to decompose into sulphur and sulphurous acid (*Fr. Mohr*, "Lehrbuch der Titrirmethode," supplement, page 384). The sulphur in hyposulphites may be determined also by conversion into sulphuric acid, in the same way as in sulphites, under similar circumstances.

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* Prepared by long-continued boiling and subsequent cooling with exclusion of air.

4. Iodic Acid.

Iodic acid may be determined by the following easy method:—distil the acid, in the free state or in combination with a base, with an excess of pure fuming hydrochloric acid, in the apparatus described in § 130, *d*, *β* (chromic acid), receive the disengaged chlorine in solution of iodide of potassium, and determine the separated iodine as directed in § 130, *d*. *β*. As 1 equivalent of iodic acid sets free 4 equivalents of chlorine, and consequently also 4 equivalents of iodine, you have to reckon 166·88 of iodic acid for 507·5 of iodine. The decomposition of iodic acid by hydrochloric acid is represented by the equation

$$IO_5 + 5\,HCl = ICl + 5\,HO + 4\,Cl.$$

(*Bunsen*, "Annal d. Chem. u. Pharm.," 86, 285.)

Second Division of the First Group of the Acids.

Sulphuric Acid; (Hydrofluosilicic Acid).

§ 132.

Sulphuric Acid.

I. Determination.

The usual, and also the best way of determining sulphuric acid is to convert it into *sulphate of baryta*. The acid may, however, be estimated also by certain volumetrical methods, based upon the insolubility of the sulphates of baryta and lead.

1. *Gravimetrical Method.*

Add to the solution, if necessary, some hydrochloric acid to acid reaction, heat to near ebullition, add chloride of barium in slight excess, and proceed as directed § 101, 1, *a*. The washing is always best effected by decantation first. Should the analysed solution contain nitric acid, some nitrate of baryta is likely to precipitate in conjunction with the sulphate; the removal of this admixture of nitrate of baryta from the precipitate requires long protracted washing with hot water. It is, under all circumstances, necessary to continue the washing of the precipitate until the last rinsings remain perfectly clear upon testing with sulphuric acid. In cases where perfect accuracy is desirable I would recommend the following proceeding after igniting and weighing the precipitate according to the directions of § 53, moisten it with a few drops of hydrochloric acid, add hot water, stir with a very thin glass rod or with a platinum wire, rinse the rod or wire, and warm gently for some time. Pour the almost clear fluid on to a small filter, and test the filtrate with sulphuric acid. If this produces turbidity or a precipitate, which is a sign that the sulphate contains an admixture of another baryta salt, wash the residue again with hot water, until the rinsings are no longer rendered turbid by sulphuric acid. Dry now the precipitate in the crucible, together with the small filter, burn the latter on the lid, heat the crucible and its contents to redness, and weigh.

2. *Volumetrical Methods.*

a. *Carl Mohr's* method ("Annal. d. Chem. u. Pharm.," 90, 165). Make a solution of baryta salt of known strength, by dissolving 1 equivalent, *i.e.*, 122·05 grm. of pure crystallized chloride of barium ($BaCl + 2\,aq.$), to 1 litre of solution, and add to the fluid to be examined for sulphuric acid—which, should it contain much free acid, is previously to be nearly neutralized with pure carbonate of soda—a measured quantity of this, best a round number of cubic centimetres, in more than sufficient proportion to precipitate the sulphuric acid, but not in too great excess. Digest the mixture for some time in a warm place, then precipitate, without previous filtration, the excess of chloride of barium with carbonate of ammonia and some pure ammonia, filter off the precipitate consisting of sulphate and carbonate of baryta, wash until the water running off acts no longer upon sensitive red litmus paper, and then determine the carbonate of baryta in the precipitate by the alkalimetrical method given in § 223. By deducting the quantity of baryta found in the state of carbonate from that corresponding to the chloride of barium added, you find the amount of baryta equivalent to the sulphuric acid present. Suppose you have added to the fluid under examination—

10 c.c. of chloride of barium solution = 0·7659 Ba O,

and found, at the end of the process,

0·300 of carbonate of baryta = 0·2331 „

the remainder, 0·5328 Ba O,

will give you the quantity of the sulphuric acid present in the examined fluid, by means of the proportion :

$$76{\cdot}59 : 40 :: 0{\cdot}5328 : x; \quad x = 0{\cdot}278 \text{ S O}_3.$$

This calculation may be considerably simplified, by estimating the carbonate of baryta, as stated in § 223, by means of a standard equivalent solution, *i.e.*, containing in the litre exactly 1 eq. of nitric acid; of which it consequently takes a volume equal to that of the chloride of barium solution to neutralize the carbonate of baryta precipitated from the latter, if no sulphuric acid is present; if, on the other hand, that acid is present, less of the nitric acid solution is required, the difference expressing the quantity of sulphuric acid. In the above example it took 3·04 cubic centimetres to neutralize the carbonate of baryta formed; deducting these from the 10 c.c. used, we have left 6·96 c.c.

$$1000 : 40 :: 6{\cdot}96 : x; \quad x = 0{\cdot}278 \text{ S C}_3.$$

The results of this method are quite satisfactory, if the solution does not contain too much free acid; but in presence of a large excess of free acid, the action of the salt of ammonia will retain carbonate of baryta in solution, which, of course, will make the amount of sulphuric acid appear higher than is really the case. That this method is altogether inapplicable in presence of phosphoric acid, oxalic acid, or any other acid precipitating baryta salt from neutral solutions, need hardly be mentioned.

b. It is often desirable, for technical purposes, to determine the sulphuric acid, in acid fluids, by the volumetrical methods. This is done by adding to the boiling solution, mixed with hydrochloric acid, chloride of barium solution of known strength (122·05 grms. of crystallized chloride of barium dissolved to 1 litre of fluid), until further addition no longer produces a precipitate. However, as it requires the use of a filtered sample to make the completion of the reaction discernible, this method is applicable only in cases where the quantity of sulphuric acid present in the fluid is already approximately known. Patience is in all cases indispensable. The precipitation of the last traces of sulphuric acid is effected by means of a decimal solution of chloride of barium. 1 c.c. of the concentrated chloride of barium solution corresponds to 0·040, 1 c.c. of the dilute (decimal) solution to 0·004 grms. of sulphuric acid.

c. In the last edition of this work I stated that in the case of fluids free from chlorine, solution of lead may be advantageously substituted for solution of chloride of barium, as sulphate of lead subsides more readily than sulphate of baryta. *Levol* ("Bulletin de la Société d'Encouragement," April, 1853—"Journ. f. prakt. Chem.," 60, 384) has recommended a modification of this method, consisting in the addition of 10 per cent. of iodide of potassium solution to the solution of the sulphate. According to this chemist, the permanent yellow coloration of the precipitate, consequent on the formation of iodide of lead, makes its appearance only after the whole of the sulphuric acid has combined with the oxide of lead. However, this is not the case if the fluids are used cold, as the iodide of lead formed where the drops of the lead solution fall into the fluid, decomposes only slowly with the alkaline sulphate. According to experiments made by *M. Grundmann*, in my own laboratory, the best results are obtained, if the solution of the sulphate, which must be neutral, is, after the addition of the iodide of potassium solution, heated in the water-bath, before the nitrate of lead solution (165·57 grms. in the litre) is added, drop by drop, until the yellow coloration remains permanent. If a corresponding experiment is then made with an approximately equal volume of a mixture of water and solution of iodide of potassium, free from sulphuric acid, and heated to the same degree, and the (inconsiderable) quantity of lead solution used to impart a yellow color to the fluid subtracted from the quantity used in the first experiment, the remainder indicates very approximately the amount of sulphuric acid present in the examined fluid (Experiment No. 82). The results obtained in this way are more satisfactory than those obtained according to *Fr. Mohr* ("Lehrbuch der Titrirmethode," part 2,77), by means of iodide of potassium paper. The method is only applicable in rare cases.

II. SEPARATION OF SULPHURIC ACID FROM THE BASES.

a. FROM THOSE BASES WITH WHICH THE ACID FORMS COMPOUNDS SOLUBLE IN WATER OR IN HYDROCHLORIC ACID.

Precipitate the sulphuric acid as in I. The filtrate contains, besides the bases originally combined with the sulphuric acid, also the excess of the chloride of barium used. The bases in the filtrate are determined by the methods given in Section V. to effect the separation of these bases from baryta.

b. FROM THOSE BASES WITH WHICH THE ACID FORMS COMPOUNDS INSOLUBLE OR DIFFICULTLY SOLUBLE IN WATER OR IN HYDROCHLORIC ACID.

α. From Baryta, Strontia, and Lime.

Fuse the finely pulverized compound under examination, in a platinum crucible, together with 5 parts of carbonate of soda and potassa. Put the crucible, with its contents, into a beaker, or into a platinum or porcelain dish, pour water over it, and apply heat until the alkaline sulphates and carbonates are completely dissolved; filter the hot solution off from the residuary carbonates of the earths, and wash the latter thoroughly with hot water. Dissolve them now in hydrochloric acid, and determine them respectively by the methods given in §§ 101, 102, and 103. Precipitate the sulphuric acid from the filtrate, as in I. Finely pulverized sulphate of lime and sulphate of strontia may be completely decomposed also by boiling with a solution of carbonate of soda or potassa; the same process will answer also for sulphate of baryta; but the operation is far more difficult, and complete decomposition is effected only by boiling the precipitate, after decanting the fluid, repeatedly with an excess of solution of carbonated alkali (*H. Rose*, "Journ. f. prakt. Chem.," 64, 382, and 65, 316).

β. *From Oxide of Lead.*

The simplest way of effecting the decomposition of sulphate of lead, is by digesting it, at the common temperature, with a solution of bicarbonate of soda or potassa, filtering, washing the precipitate, determining the sulphuric acid in the filtrate, as in I., dissolving the precipitate, which contains alkali, in nitric acid or acetic acid, and determining the lead in the solution, by one of the methods given in § 162.

Presence of strontia and lime necessitates no alteration in this method; but if baryta also is present, and it is accordingly necessary to ignite the mixture (safest in a porcelain crucible), with carbonated alkalies, or to boil repeatedly with an excess of solution of the same, the alkaline filtrate contains always some lead, which must be precipitated by transmitting carbonic acid gas through it.

Supplement to the Second Division.

§ 133.

HYDROFLUOSILICIC ACID.

If you have hydrofluosilicic acid in solution, add solution of chloride of potassium, or chloride of sodium, then a volume of strong alcohol equal to the fluid to be operated upon, filter the precipitated silicofluoride of potassium or sodium on a weighed filter, and wash with a mixture of equal volumes of spirit of wine and water. Dry the washed precipitate at 212° F., and weigh. Mix the alcoholic filtrate with hydrochloric acid, evaporate to dryness, and treat the residue with hydrochloric acid and water. If this leaves an undissolved residue of silicic acid, this is a sign that the examined acid contained an excess of silicic acid; the weight of the residue shows the amount of the excess.

Silicofluoride of potassium has the formula $K\,Fl, Si\,Fl_2$, silicofluoride of sodium, $Na\,Fl, Si\,Fl_2$. Both compounds are anhydrous at 212° F. They dissolve with difficulty in water, and are insoluble in dilute spirit of wine. The analysis of silicofluorides of metals is best effected by heating in platinum vessels, with concentrated sulphuric acid; fluoride of silicon and hydrofluoric acid volatilize, the bases are left behind in the form of sulphates, and may, in many cases, after volatilization of the excess of sulphuric acid, be weighed as such. If the metallic silicofluorides to be analyzed contain water, mix them most intimately with 6 parts of recently ignited oxide of lead, cover the mixture, in a small retort, with a layer of pure oxide of lead, weigh the retort, heat cautiously until the contents begin to fuse together, remove the aqueous vapor still remaining in the vessel by suction, and weigh the retort again when cold. The diminution of weight shows the quantity of water expelled. Do not neglect testing the drops of the escaping water with litmus paper; the result is accurate only if they have no acid reaction; compare § 35, γ.

Third Division of the First Group of the Acids.

PHOSPHORIC ACID—BORACIC ACID—OXALIC ACID—HYDROFLUORIC ACID.

§ 134.

1. PHOSPHORIC ACID.

I. DETERMINATION.

Tribasic phosphoric acid may be determined in a great variety of ways. The forms in which this determination may be effected have been given already in § 93, 4. The most appropriate forms for the purpose, however, are *pyrophosphate of magnesia* and *phosphate of sesquioxide of uranium*. The method based upon the conversion of the acid into these forms is applicable in almost all cases. The determination as pyrophosphate of magnesia is frequently preceded by precipitation as phosphate of binoxide of tin, phosphate of suboxide of mercury, or phospho-molybdate of ammonia. The other forms in which phosphoric acid may be determined give also, for the most part, very good results, but admit only of limited application. Volumetrical methods also have been recommended; but they still leave much to be desired.

With regard to metaphosphoric acid and pyrophosphoric acid, I have simply to remark here that these acids cannot be determined by any of the methods given below. The best way to effect their quantitative analysis is to convert them into tribasic phosphoric acid; as follows:—

α. *In the dry way.* By protracted fusion with from 4 to 6 parts of carbonate of soda and potassa. This method is, however, applicable only in the case of metaphosphates and pyrophosphates of the alkalies, and of those metaphosphates or pyrophosphates of metallic oxides which are completely decomposed by fusion with alkaline carbonates; it fails, accordingly, for instance, with compounds of metaphosphoric or pyrophosphoric acid with the alkaline earths, except magnesia.

β. *In the humid way.* The salt is heated for some time with a strong acid, best with concentrated sulphuric acid (*Weber*, "Pogg. Annalen," 73, 137). This method leads only to the attainment of approximate results, in the case of all salts whose bases form soluble compounds with the acid added, since in these cases the metaphosphoric or pyrophosphoric acid is never completely liberated; but the desired result may be fully attained by the use of any acid which forms insoluble compounds with the bases of the meta- or pyrophosphates under examination. Respecting the partial conversion in the former case. I have found that it approaches the nearer to completeness the greater the quantity of free acid added,* and that the ebullition must be long continued (compare Experiment No. 36).

Bunce's statement that phosphoric acid volatilizes when a phosphate is evaporated to dryness with hydrochloric or nitric acid, and the residue heated a little (*Sillim.* Journ. May, 1851, p. 405), is quite erroneous (compare my paper on the subject, in "Annal. der Chem. und Pharm.," 86, 216). But, on the other hand, it must be borne in mind that tribasic phosphoric acid under these circumstances changes, not indeed at 212° F., but at a temperature still below 302° F., to pyrophosphoric acid; thus, for instance, upon evaporating common phosphate of soda with hydrochloric acid in excess, and drying the residue at 302° F., we obtain $\check{N}a\,Cl + P\,O_5, Na\,O, H\,O$.

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* There are, however, certain considerations also which forbid going too far in this respect.

a. Determination as Phosphate of Lead.

Proceed as with arsenic acid, § 127 (evaporate with a weighed quantity of oxide of lead, and ignite). This method presupposes that no other acid is present in the aqueous or nitric acid solution; it has this great advantage that it gives accurate results, no matter whether the phosphoric acid present is mono-, bi-, or tribasic.

b. Determination as Pyrophosphate of Magnesia.

α. *Direct determination* (suitable in all cases in which it is quite certain that the acid is present in the tribasic state, either free or combined with an alkali).

Add to the solution a clear mixture of sulphate of magnesia, chloride of ammonium, and ammonia (see § 62, 7), as long as a precipitate continues to form; should the solution not yet evolve a strong ammoniacal odor, add some more ammonia; let the mixture stand 12 hours, without applying heat, filter, wash the precipitate with a mixture of 3 parts of water and 1 part of solution of ammonia, until the rinsings, after the addition of hydrochloric acid, are no longer rendered turbid by chloride of barium, and proceed afterwards exactly as directed in § 104, 2. The results are very accurate (Experiment No. 83). The loss sustained from the slight solubility of the basic phosphate of magnesia and ammonia is very trifling (Experiment No. 32), and may even be altogether compensated by measuring the filtrate and rinsings, and adding for every 54 cubic centimetres 0·001 grm. of pyrophosphate of magnesia. For the properties of the precipitate and residue, see § 74. If the solution contains pyrophosphoric acid, the precipitate is flocculent, and dissolves in ammoniated water (*Weber*).

β. *Indirect determination*, after previous precipitation as phosphomolybdate of ammonia (*Sonnenschein*, "Journal für prakt. Chem.," 53, 343). Applicable in all cases in which the phosphoric acid is present in the tribasic state, even in presence of alkaline earths, alumina, sesquioxide of iron, &c.

Dissolve 1 part of molybdic acid in 8 parts of solution of ammonia, mix this with 20 parts of nitric acid, and add of the mixture to the nitric acid solution of the phosphates sufficient to make the quantity of molybdic acid contained in the amount added about 40 times that of the phosphoric acid contained in the phosphate. The large proportion of molybdic acid required sufficiently indicates the necessity of preparing a rather considerable quantity of solution. Digest the fluid, with the yellow precipitate formed in it, 24 hours, on the water-bath, and wash the precipitate with the same solution of molybdic acid with which the precipitation has been effected. Let the filtrate stand some time on the water-bath, to see whether a further precipitate will form, and if so, add this precipitate to the first. Proof that the molybdic acid has been used in excess, may, indeed, also be obtained by adding to a drop of the fluid, previously to filtration, sulphuretted hydrogen water which must produce a brown precipitate of sulphide of molybdenum; this proceeding, however, does not afford the same security against incomplete precipitation as the former. Dissolve the precipitate, on the filter, in ammonia, and precipitate the phosphoric acid with magnesia mixture (compare *a*). The results are accurate (compare also *Craw*, "Pharm. Centralblatt," 23, 669). Instead of the nitric acid solution of molybdic acid, a solution of the latter in hydrochloric acid may be used, prepared by adding to a solution of molybdate of ammonia containing 5 per cent. of molybdic acid, hydrochloric acid, until the precipitate which forms at first is redissolved. This hydrochloric acid solution is then used to precipitate and wash in the same way as the nitric acid solution.

As this method requires so large a quantity of molybdic acid, it is usually resorted to only in cases where methods *b*, *a*, and *c* are inapplicable; the amount of phosphoric acid in the quantity of substance taken to operate upon must not exceed 0·1 grm. Arsenic acid and silicic acid,* if present, must first be removed.

γ. *Indirect determination*, after previous precipitation as phosphate of suboxide of mercury (*H. Rose*, "Pogg. Ann.," 76, 218).

Dissolve the phosphate in neither too large nor too small a quantity of nitric acid, in a porcelain dish of proper size, add to the solution pure metallic mercury in sufficient quantity to leave a portion, even though only a small one, undissolved by the free acid. Evaporate on the water-bath to dryness. If the warm mass still evolves an odor of nitric acid, moisten it with water, and heat again on the water-bath, until it smells no longer of nitric acid. Add now hot water, pass through a small filter, and wash until the rinsings leave no longer a fixed residue upon platinum. Dry the filter, which, besides the phosphate, contains also basic nitrate of suboxide of mercury and free mercury, mix its contents, in a platinum crucible, with carbonate of soda and potassa in excess, roll the filter into the shape of a ball, place it into a hollow made in the mixture, and cover the whole with a layer of carbonate of soda and potassa. Expose the crucible, under a chimney with good draught, for about half an hour to a moderate heat, so that it does not get red-hot. At this temperature, the nitrate of suboxide of mercury and the metallic mercury volatilize. Heat now over the lamp to the most intense ignition, and treat the residue with hot water, which will dissolve it completely, if no sesquioxide of iron was present. Supersaturate the clear (if necessary, filtered) solution with hydrochloric acid, add ammonia and magnesia mixture, and proceed as in *a*. This method may be applied to effect the separation of phosphoric acid from all bases, except alumina; compare also § 135, 1.

δ. *Indirect determination*, after previous precipitation as phosphate of binoxide of tin (*W. Reissig*).†

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* Silicic acid also is thrown down, in form of a yellow precipitate, by acid solution of molybdate of ammonia, especially in presence of much chloride of ammonium (*W. Knop*, "Chem. Centralb.," 1857, 691). Mr. *Grundmann*, who repeated *Knop's* experiments in my laboratory, obtained the same results. The precipitate dissolves in ammonia. If the solution, after addition of some chloride of ammonium, is allowed to stand for some time, the silicic acid separates, and the phosphoric acid may then be precipitated from the filtrate with magnesia mixture; it is, however, always the safer way to remove the silicic acid first.

† "Annal. d. Chem. u. Pharm.," 98, 339. The method is a judicious modification of *Reynoso's* process ("Journ. f. prakt. Chem.," 54, 261), which latter, though in prin-

Dissolve the substance in which the phosphoric acid is to be estimated in concentrated nitric acid, add, at least, eight times as much tinfoil as there is phosphoric acid present, and warm the mixture for five or six hours, until the precipitate has completely subsided, leaving the supernatant fluid quite clear. Wash by decantation combined with filtration, rinse the washed precipitate into a platinum dish, and digest with a small quantity of highly concentrated solution of potassa. The product of this operation is a mixture of metastannate and phosphate of potassa, which, upon addition of hot water, dissolves to a clear fluid, and even very readily if there has not been too much hydrate of potassa used. Dissolve, in the same way, the trifling particles of the precipitate which may still adhere to the filter, add this solution to that of the precipitate, transfer the whole fluid to a weighed flask of 1000 grammes capacity, and dilute with water to make the fluid up to about 900 grammes; saturate now with sulphuretted hydrogen, adding also some pentasulphide of ammonium, and then acetic acid, until the bisulphide of tin is precipitated, and the fluid *slightly* acid. Replace the flask now on the scale, add water, until the contents weigh 1000 grammes (or some other round number), shake, allow it to stand from 12 to 16 hours, filter the supernatant clear fluid into a porcelain dish, and weigh the flask again, which now contains the rest of the fluid, together with the sulphide of tin. The weight found gives, by simple subtraction, also the quantity of the filtrate in which the phosphoric acid is to be estimated. The proportion which this bears to the total quantity of the fluid, viz., 1000 grammes, minus the weight of the sulphide of tin (which may be calculated with sufficient accuracy from the amount of tin originally used, or may be estimated in the direct way), is easily found.

Wash the filter used in transferring the clear fluid from the flask to the porcelain dish, and add the rinsings to the filtrate in the latter; evaporate the fluid until a small quantity only is left, and then estimate the phosphoric acid in this according to the directions of *b*, *α*. The way here recommended of effecting the separation of the phosphoric acid fluid from the sulphide of tin must be resorted to of necessity, since in the filtration and washing of the sulphide, no matter whether with pure water or water containing sulphuretted hydrogen, a small quantity of tin would inevitably be dissolved. Results accurate.

c. Determination as Phosphate of Sesquioxide of Uranium.

Leconte, *A. Arendt*, and *W. Knop's* method,[*] very suitable in presence of alkalies and alkaline earths, but not in presence of any notable amount of alumina; in presence of sesquioxide of iron, the method can be applied only with certain modifications (see § 135, *h*, *γ*). Dissolve the phosphate under examination in acetic acid. If you have a nitric or hydrochloric acid solution, remove the greater portion of the free acid by evaporation, add ammonia until red litmus paper dipt into it turns very distinctly blue, and then redissolve the precipitate formed in acetic acid;

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ciple free from defects, yet presents certain practical difficulties, owing principally to the large proportion of tin foil required for the process (eight times the quantity of the phosphoric acid), which makes the presence of even slight impurities in the tin a source of considerable error. These remarks of *Reissig* completely coincide with the results of my own experiments.

[*] *Leconte* was the first to recommend the method of precipitating phosphoric acid from acetic acid solution by means of a salt of uranium ("Jahresb." von *Liebig* und *Kopp*, 1853, 642); *A. Arendt* and *W. Knop* have subsequently subjected it to a careful and searching examination ("Chem. Centralbl.," 1856, 769, 803, and 1857, 177).

if mineral acids were present, add also some acetate of ammonia. Mix the fluid now with solution of acetate of sesquioxide of uranium, and heat the mixture to boiling, which will cause the phosphoric acid to separate, in form of yellow phosphate of sesquioxide of uranium and ammonia.

Wash the precipitate by decantation combined with filtration, taking care to boil the mixture after every fresh addition of water; the operation may be materially facilitated, by adding, immediately after precipitation, as soon as the liquid has cooled a little, 2 or 3 drops of chloroform, and giving the mixture a vigorous shake, or boiling it once or twice. Dry the precipitate, and ignite as directed § 53. It is advisable to moisten the ignited mass with nitric acid, and then ignite once more. For the properties of the precipitate and residue, see § 93, *e*. Should it be necessary to dissolve the ignited residue again, for the purpose of reprecipitating it, this can be done only after fusing it previously with a large excess of carbonate of soda and potassa, and thereby converting the pyrophosphoric into tribasic phosphoric acid. Results accurate; compare Experiment No. 84.

d. Determination as Basic Phosphate of Sesquioxide of Iron.

α. Proceed exactly as in the determination of arsenic acid as arsenate of sesquioxide of iron, by *Kobell's* modification of *Berthier's* method (§ 127, 3, *b*). The results are accurate.

β. Mix the acid fluid containing the phosphoric acid with an excess of solution of sesquichloride of iron of known strength, add, if necessary, sufficient alkali to neutralize the greater portion of the free acid, mix with acetate of soda in excess, and boil. If the quantity of solution of sesquichloride of iron added was sufficient, the precipitate must be brownish-red. This precipitate consists of basic phosphate and basic acetate of sesquioxide of iron, and contains the whole of the phosphoric acid and of the sesquioxide of iron. Filter off boiling, wash with boiling water mixed with some acetate of ammonia, dry carefully, and ignite in a platinum crucible with access of air (§ 53). Moisten the residue left upon ignition with strong nitric acid, evaporate this at a gentle heat, and ignite again. Should this operation have increased the weight, which, however, is not usually the case, it must be repeated, until the weight remains constant. Deduct from the weight of the residue that of the sesquioxide of iron contained in the solution added; the difference is the phosphoric acid.

This modification of *Schulze's* method was first recommended by *A. Müller* ("Journ. f. prakt. Chem.," 47, 341); it has been adopted also by *Way* and *Ogston*, in their analyses of ashes ("Journal of the Royal Agricultural Society," VIII. Part I.). By the use of a solution of sesquichloride of iron of known strength, the estimation of the sesquioxide of iron in the residue (which would have to be effected in the manner described § 113, 2, *a*), is dispensed with.

γ. J. Weeren's method, suitable for the estimation of the phosphoric acid in phosphates of the alkalies and alkaline earths ("Journ. f. prakt Chem.," 67, 8). Mix the nitric acid solution of the phosphate under examination, which must contain no other strong acid, with a solution of nitrate of sesquioxide of iron of known strength, in sufficient proportion to ensure the formation of a basic salt; evaporate the mixture to dryness, heat the residue to 320° F., until no more nitric acid fumes escape, treat with hot water until all nitrates of the alkalies and alkaline earths are removed,* collect the ochreous precipitate on a filter, dry, ignite (§ 53), weigh, and deduct from the weight the quantity of sesquioxide of iron added.

e. Determination as Basic Phosphate of Magnesia ($3\,MgO, PO_5$). *Fr. Schulze's* method, suitable more particularly to effect the separation of phosphoric acid from the alkalies ("Journ. f. prakt. Chem.," 63, 440).

Mix the solution of the alkaline phosphate, which contains chloride of ammonium, with a weighed excess of pure magnesia, evaporate to dryness, ignite the residue until the chloride of ammonium is expelled, and separate the magnesia, which is still present in form of chloride of magnesium, by means of oxide of mercury (§ 104, 3, *b*). Treat the ignited residue with water, filter the solution of the chlorides of the alkali metals, wash the precipitate, dry, ignite, and weigh. The excess of weight over that of the magnesia used shows the quantity of the phosphoric acid present in the analysed phosphates. Results satisfactory.

f. Determination as Phosphate of Silver, see § 135, *a*.

g. Determination by Volumetric Analysis.

Although it would be most desirable to have a good volumetrical method for determining phosphoric acid, considering how very often the analyst has to determine this acid, yet, up to the present time, this object remains still unattained. Certain methods have, indeed, been proposed, but they lead only to an approximative estimation of the acid, and are accordingly used only in the analysis of urine, for want of more definite and accurate processes. They are based upon the insolubility of phosphate of sesquioxide of iron (Fe_2O_3, PO_5) in acetic acid, or also in a hydrochloric acid solution mixed with an excess of acetate of soda. *Liebig* ("Annal. d. Chem. u. Pharm.," 78, 150) recommends to acidify the phosphoric acid fluid with acetic acid, and to add acetate of soda, then the least excess of a solution of known strength of sesquichloride of iron, free from acid, or iron alum. The point when the iron solution has been added just in sufficient excess, is ascertained by pressing, some time after the last addition, a glass rod moistened with the fluid against a double filter paper, laid on another filter paper, moistened with solution of ferrocyanide of potassium and resting on a porcelain plate. If the iron solution has been added in excess, a blue color will make its appearance in a few seconds. The great difficulty in this process, which otherwise has the advantage of promptness in its favor, is to hit this point with a proper degree of exactness. The most effective way is to take, to about 0·2 grm. of phosphoric acid, 10 cubic centimetres of concentrated acetic acid and a sufficient quantity of acetate of soda.—*Räwsky* ("Journ. f. prakt. Chem.," 41, 365) recommends the following method: add to the acid solution (which, with the exception of sesquioxide of iron, must contain no bases forming with phosphoric acid compounds insoluble in acetic acid), ammonia, until the free acid is nearly neutralized, then acetate of sesquioxide of iron† in the least possible excess. The phosphate of sesquioxide of iron is deposited in the form of a faintly yellowish white precipitate. Filter, and wash carefully with cold water—an operation which in the case of larger quantities of substance takes much time;

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* In presence of magnesia, warming with a solution of nitrate of ammonia is advisable.

† A solution of iron alum (1:10), mixed with an equal quantity of solution of acetate of soda (1: 10), and to which it is as well to add some free acetic acid, answers the same purpose.

dissolve the precipitate in hydrochloric acid, and determine the iron in the solution in the manner directed § 113, 2, *a*. *Räwsky* proceeds upon the assumption that the precipitate has the composition PO_5, Fe_2O_3, and calculates for every 700 of iron 900 (rigorously 887·5, the equivalent of phosphorus being 387·5) of phosphoric acid. This assumption is not correct, however, as the proportion of iron in the precipitate varies, being the higher, the greater the excess of solution of iron used.

For a more detailed account of these methods, I refer to *Neubauer* and *Vogel's* "Anleitung zur Analyse des Harns," second edition, page 109; and *Dunklenberg's* paper on the subject, in "Annal. d. Chem. u. Pharm.," 93, 88.

II. SEPARATION OF PHOSPHORIC ACID FROM THE BASES.

§ 135.

a. From the Fixed Alkalies (see also *b, e, l, m*).

α. The method I., *d*, in one of its modifications, is resorted to, or method I., *e*. The alkalies are found in the filtrate as nitrates or chlorides.

β. The method I., *b*, *α*, is applied, and the separation of the magnesia from the alkalies in the filtrate is effected in the manner described § 153.

γ. Salts composed after the formula $3MO, PO_5$ are dissolved in water and the solution is precipitated with neutral solution of silver; the yellow precipitate formed $3AgO, PO_5$, is washed, dried, and ignited in the manner described § 53.

Phosphates composed after the formula $2MO, HO, PO_5$, are ignited, the residue dissolved in water, and precipitated with neutral solution of silver. The fluid is filtered off from the precipitate, which, in this case, consists of pyrophosphate of silver $2AgO, PO_5$, and the latter washed, dried, and ignited (§ 53). For the properties of the precipitated phosphates of silver, see § 93, 4.

The bases in the filtrates are determined after the removal of the excess of silver (see § 162).

The results are accurate; this method is particularly convenient, on account of the facility with which the alkalies may be estimated in the filtrate.

b. From the whole of the Alkalies see also (*a, e, l, m*).

α. The separation of the phosphoric acid is effected by the method described § 134, *d*, *α*, and the baryta and the alkalies in the filtrate are separated as directed § 153.

β. The aqueous solution is mixed with acetate of lead in slight excess, and the precipitate formed allowed to subside; the fluid is then filtered off, and the alkalies in the filtrate are separated from the excess of the salt of lead used in the process, as directed in § 162. The quantity of the phosphoric acid originally present in the analysed compound may be calculated from the loss; but it may also be determined in the direct way, by treating the washed precipitate of phosphate of lead according to § 135, *c*.

c. From Baryta, Strontia, Lime, and Oxide of Lead.

The compound under examination is dissolved in hydrochloric or nitric acid, and the solution precipitated with sulphuric acid in slight excess. In the separation of phosphoric acid from strontia, lime, and oxide of lead, alcohol is added with the sulphuric acid. The phosphoric acid in the filtrate is determined according to § 134, *b*, *a* (in the case of strontia, lime, and oxide of lead, after previous removal of the alcohol by evaporation). The determination of the phosphoric acid is effected with the most accurate results by saturating the fluid with carbonate of soda, evaporating to dryness, and fusing the residue with carbonate of soda and potassa. The fused mass is then dissolved in water, and the further process conducted as in § 134, *b*, *a*.

d. From Magnesia (see also *e*, *i*, *l*, and *m*).

The phosphoric acid is separated as in § 134, *d*, *a*; and the magnesia and baryta in the filtrate are separated in the manner described § 154.

e. From the whole of the Alkaline Earths (comp. also § 135, *i*, *l*, and *m*).

a. Separate phosphoric acid as phosphate of sesquioxide of uranium, as directed in § 134, *c*, and the sesquioxide of uranium from the alkaline earths, in the filtrate, according to the directions given in the supplement to §§ 160 and 161. This is an excellent method.

β. The phosphoric acid is separated by one of the methods given in § 134 *d*, *β* and *γ*. If the method *d*, *β* is applied, the alkaline earths remain in solution as chlorides with the alkaline acetate and alkaline chloride; if *d*, *γ*, they are obtained in solution as nitrates. The results are satisfactory.

γ. Dissolve in the least possible amount of nitric acid, add acetate of lead in slight excess, let the precipitate formed subside, and filter; wash the precipitate, which consists of phosphate and basic nitrate of lead, dry, ignite (§ 53), and weigh. The residue is phosphate of lead + oxide of lead, or in other terms, phosphoric acid + x oxide of lead. Put the crucible, with its contents, into a beaker, pour moderately dilute nitric acid over it, and warm, until solution is effected; then decant the fluid into another glass, wash, add the rinsings to the solution, and determine the oxide of lead in it as sulphate (§ 116, 2). Calculate from this the oxide of lead, and deduct the result from the weight of the first residue: the difference gives the quantity of the phosphoric acid. In the fluid filtered off from the first precipitate, the bases are separated from the excess of the salt of lead used, in the manner described (§ 162). This method also gives satisfactory results.

f. From Alumina (see also § 135, *i*, and *m*.)

a. (*Otto* and *Fresenius*, applicable also in presence of sesquioxide of iron.) Dissolve in hydrochloric or nitric acid, dilute a little, add a tolerable quantity of tartaric acid, and then ammonia in excess. If you have added sufficient tartaric acid, the fluid must now appear clear. Add, in slight excess, a clear solution of sulphate of magnesia mixed with chloride of ammonium and ammonia, and let the mixture stand at rest for 12 hours; then filter, and wash the precipitate with dilute solution of ammonia; to free it completely from alumina, redissolve it in hydrochloric acid, add a little tartaric acid, and reprecipitate with ammonia. Treat the precipitate now as directed in § 134, *b*, *a*. To obtain the alumina contained in the filtrate, add some nitrate of potassa and a sufficient quantity of carbonate of soda to effect the decomposition of the chloride of ammonium,* evaporate to dryness, and ignite the residue in a platinum vessel. Dissolve in nitric or hydrochloric acid by continued application of heat, and separate the alumina from the magnesia as directed in § 156.

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* The ignition of alumina in presence of chloride of ammonium would entail loss by the formation and escape of chloride of aluminium (*H. Rose*).

β. (*Berzelius.*) Pulverize the compound very finely, mix the powder with about 1½ parts of pure silicic acid* and 6 parts of carbonate of soda, in a platinum crucible, and expose for half an hour to a strong red heat. Treat the ignited mass with water, add bicarbonate of ammonia in excess, digest for some time, then filter and wash. On the filter you have now silicate of alumina and soda, in the solution phosphate of soda, bicarbonate of soda, and carbonate of ammonia, (were the solution filtered before the addition of the bicarbonate of ammonia, it would contain also some of the alumina compound). Determine the phosphoric acid in the solution as directed in § 134, *b*, *a*, and separate and determine the alumina in the insoluble residue in the manner described § 140.

γ. (*Fuchs.*) Dissolve in solution of potassa, and add solution of silicate of potassa. Dilute the mucilaginous mass, which forms, with water, and boil. Filter off the precipitate of silicate of alumina and potassa. The filtrate contains the whole of the phosphoric acid. Acidify it with hydrochloric acid, and separate the phosphoric acid and silicic acid in the manner described in § 166.

δ. (*Wackenroder* and *Fresenius.*) Precipitate the acid solution with ammonia, taking care not to use a great excess of that reagent, and add chloride of barium as long as a precipitate continues to form. Digest for some time, and then filter. The precipitate contains the whole of the alumina and the whole of the phosphoric acid; the latter combined partly with alumina, partly with baryta. Wash it a little, and dissolve in the least possible quantity of hydrochloric acid. Saturate the solution, at a high temperature, with carbonate of baryta, add solution of soda in excess, apply heat, precipitate the baryta which the solution may contain with carbonate of soda, and filter. You have now the whole of the alumina in the solution, the whole of the phosphoric acid in the precipitate. Acidify the solution with hydrochloric acid, boil with some chlorate of potassa, and precipitate as directed § 105. Dissolve the precipitate in hydrochloric acid, precipitate the baryta with dilute sulphuric acid, filter, and determine the phosphoric acid in the filtrate by precipitation with solution of magnesia in the manner described in § 134, *b*. *a*. *Hermann* has applied a similar method in his analysis of Gibbsite.

g. *From Sesquioxide of Chromium* (see also *i*, *l*, and *m*).

Fuse with carbonate and nitrate of soda, and separate the chromic acid and phosphoric acid in the manner described § 166.

h. *From the Metallic Oxides of the Fourth Group* (see also *i*, *l*, and *m*).

a. Fuse with carbonate of soda and potassa. Keep in fusion for some time, and then boil the fused mass with water. Filter and wash the undissolved residue. The filtrate contains the phosphoric acid combined with soda; determine the acid as directed in § 134, *b*, *a*. Dissolve the residue, which generally retains an admixture of alkalies, in acid, and determine the respective metals in the solution by the appropriate methods (see §§ 108 to 114).

In the case of phosphate of manganese, carbonate of soda is used instead of carbonate of soda and potassa. Should a small portion of manganic acid have got into the solution, this is removed by a little sulphuretted hydrogen water. In the case of phosphate of sesquioxide of iron, it often happens that complete separation is not effected by this method.

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* The safest way is to use artificially prepared silicic acid.

β. Dissolve in hydrochloric acid, add tartaric acid, then ammonia, and finally, in a flask which is to be closed afterwards, sulphide of ammonium, put the flask in a moderately warm place; allow the mixture to deposit until the fluid appears of a yellow color, without the least tint of green; filter, and determine the metals as directed in §§ 108 to 114. The phosphoric acid is calculated from the loss, or determined according to § 134, *b*, *a*. The magnesia mixture may immediately be added to the filtrate, which contains sulphide of ammonium. The washed precipitate is once more dissolved, and the solution reprecipitated as in *f*, *a*. This method is not well adapted for the analysis of the phosphate of nickel.

γ. Special method for effecting the separation of phosphoric acid from the oxides of iron. *R. Arendt* u. *W. Knop*, "Chem. Centralbl.," 1857, 182.) Dissolve in hydrochloric acid to the least possible volume of fluid, add to the clear solution protochloride of uranium,[*] until the color inclines distinctly to green, and a drop of sulphocyanide of potassium no longer produces a red tint in the fluid. Add now ammonia to distinct alkaline reaction, then acetate of sesquioxide of uranium, and free acetic acid, together with a few drops of solution of acetate of protoxide of uranium,[†] and heat to boiling. The color of the mixture must appear distinctly greenish, and not dirty. Let the solid particles *completely* subside, and then decant on to a filter; boil the precipitate with water and some chloride of ammonium, and decant again. Repeat this operation once more, and then treat the precipitate as directed in § 134, *c*. Separate the uranium and iron in the filtrate as directed in the supplement to §§ 160 and 161. The results are satisfactory. The addition of the protochloride of uranium has for its object the reduction of the sesquichloride of iron to protochloride.

δ. (Special method for effecting the separation of phosphoric acid from the oxides of iron, *Fresenius*.) Reduce the sesquioxide of iron in the solution, if necessary, with sulphite of soda, add pure hydrate of potassa in excess, boil until the precipitate has become black and granular, filter, and wash with boiling water. The precipitate on the filter is protosesquioxide of iron, free from phosphoric acid. The phosphoric acid in the filtrate is determined as directed in § 134, *b*, *a*.

i. *From Metallic Oxides of the Second, Third, and Fourth Groups.*

a. More especially from the alkaline earths, alumina, the protoxides of manganese, nickel, and cobalt, and oxide of zinc; also from sesquioxide of iron, if the quantity of the latter is not too considerable.

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[*] *Preparation of the Protochloride of Uranium.*—Dissolve carbonate of sesquioxide of uranium and ammonia in double the quantity of hydrochloric acid required to effect solution, add a few drops of solution of bichloride of platinum, and throw into the mixture an excess of fine copper turnings. Heat, and let the mixture boil from 10 to 15 minutes. The fluid speedily acquires a green color, and the conversion of the chloride to subchloride is soon effected. To separate the dissolved subchloride of copper, let the mixture boil until water produces a copious precipitate in a sample of it. When this point is attained, dilute the entire solution, allow it to cool, filter off the subchloride of copper, transmit through the filtrate sulphuretted hydrogen in excess; filter off the precipitated subsulphide of copper, mix the solution with chloride of ammonium, and boil until all sulphuretted hydrogen has escaped. *R. Arendt* u. *W. Knop*, "Chem. Centralb.," 1857, 164.

[†] *Preparation of Acetate of Protoxide of Uranium.*—Precipitate solution of protochloride of uranium with ammonia, and dissolve the precipitate in acetic acid, best at a high temperature.

The phosphoric acid is precipitated as phosphate of binoxide of tin, according to the directions of § 134, *b*, *δ*. The filtrate contains the bases free from all foreign bodies, which, of course, greatly facilitates their estimation. *Reissig* obtained very satisfactory results by this method.

β. From sesquioxide of iron, alkaline earths, and all other oxides not precipitable by carbonate of baryta (*H. Rose's* method).

Mix the hydrochloric acid solution—after removing the free acid as far as practicable, by evaporation, and neutralizing it partly by carbonate of soda—with carbonate of baryta in excess, let the mixture digest some days, in the cold, filter, and wash with cold water. The precipitate contains the whole of the phosphoric acid in combination with sesquioxide of iron, alumina, baryta, and besides also the excess of carbonate of baryta used. The other bases are in the filtrate. The precipitate is dissolved in the least possible quantity of dilute hydrochloric acid, the baryta cautiously precipitated with sulphuric acid, the fluid saturated with carbonate of soda, and evaporated to dryness with the precipitate in it; the residue is mixed with an equal quantity of pure silicic acid, and six times as much carbonate of soda, and the mixture heated in a large platinum crucible, commencing with a gentle heat, which is then gradually increased to a very high degree of intensity. The remaining operations are conducted exactly as directed in § 135, *f*, *β*.

γ. *From sesquioxide of iron in large proportion and in presence of alkaline earths.* (*Fresenius*, "Journ. f. prakt. Chem.," 45, 258).

The determination of the phosphoric acid in such compounds may, indeed, be accomplished by the method given in § 134, *d*, but the separation by these methods, of a small quantity of phosphoric acid from a very large proportion of sesquioxide of iron is a most tedious operation; it is therefore preferable in cases of the kind to proceed as follows: the hydrochloric acid solution is heated to boiling, then removed from the lamp, and solution of sulphite of soda added, until carbonate of soda produces a nearly white precipitate; the mixture is then boiled until the odor of sulphurous acid has gone off; the excess of free acid which might still be present is nearly neutralized with carbonate of soda, a few drops of chlorine water are added, and lastly, acetate of soda in excess. The minutest quantity of phosphoric acid shows itself at once by the formation of a white precipitate of phosphate of sesquioxide of iron.* More chlorine water is now added, drop by drop, until the fluid appears reddish; it is then boiled until the precipitate has well subsided; the latter is filtered off hot, and washed with hot water mixed with a little acetate of ammonia. The precipitate contains the whole of the phosphoric acid, together with a small portion of the iron; the filtrate contains the greater portion of the latter, together with the alkaline earths. The precipitate is treated as directed § 135, *h*. If free from alumina, it may also be ignited, weighed, and the iron in it determined in the volumetrical way (§ 113), in which case the phosphoric acid is calculated from the loss. If, on the other hand, the precipitate contain alumina, the iron may be separated as protosesquioxide, according to the directions of § 135, *h*, *δ*, and the alumina and phosphoric acid in the filtrate, according to § 135, *f*, *a*; or the latter method of separating the phosphoric acid may be applied first, and the alumina and sesquioxide of iron separated after.

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* Silicic acid and arsenic acid produce a similar precipitate, and must therefore, if present, be previously removed.

k. From the Metals of the Fifth and Sixth Groups.

Dissolve in hydrochloric or nitric acid, precipitate with sulphuretted hydrogen, filter, determine the bases by the methods given in §§ 115 to 127, and the phosphoric acid in the filtrate by the method described § 134, *b*, *a*. From oxide of silver the phosphoric acid is separated in a more simple way still, by adding hydrochloric acid to the nitric acid solution; from oxide of lead it is separated most readily by the method described in § 135, *c*.

l. From all Bases, except Alumina and Oxide of Mercury (H. Rose).

The phosphoric acid is separated as phosphate of suboxide of mercury by *Rose's* method (§ 134, *b*, *γ*).

a. If the substance contained no iron, the fluid filtered off from the phosphate of suboxide of mercury contains all the bases as nitrates, together with much nitrate of suboxide of mercury, and occasionally also some oxide. The former is removed by the addition of hydrochloric acid. The precipitated subchloride of mercury is free from other bases. If only a slight precipitate is produced by hydrochloric acid, the filtration is preceded by addition of ammonia. The bases in the filtrate are determined in the usual way. If the mercury has been separated by ammonia, the precipitate is dried and ignited (under a chimney with good draught). Should a residue remain, this must be more closely examined. If it consists of phosphates of the alkaline earths, the treatment with mercury and nitric acid must be repeated; if, on the contrary, it consists of pure magnesia or of carbonates of the alkaline earths, it is dissolved in hydrochloric acid, and the solution added to the fluid containing the chief portion of the bases. The following method is often advantageously resorted to instead of the one just described; the fluid filtered off from the phosphate of suboxide of mercury is evaporated to dryness, in a platinum dish, and the residue ignited, in a platinum crucible, under a chimney with good draught. If alkaline nitrates are present, some carbonate of ammonia must be added from time to time during the process of ignition, to guard against injury to the crucible from the formation of caustic alkali. The ignited residue is treated, according to circumstances, first with water and then with nitric acid, or at once with nitric acid.

β. If the substance contained iron, the greater part of that metal is left undissolved with the phosphate of suboxide of mercury. The dissolved part is separated from the other bases by the methods given in Section V.; the undissolved part is obtained, after ignition of the residue, with carbonate of soda and potassa, and treating the ignited mass with water, in the form of sesquioxide of iron containing alkali. This is dissolved in hydrochloric acid, and the solution precipitated with ammonia. As alumina cannot be decomposed, like sesquioxide of iron, by fusion with carbonate of soda and potassa, whilst nitrate of alumina and nitrate of sesquioxide of iron are both equally decomposed by simple evaporation the method just described is not applicable in presence of alumina.

m. From all Bases without exception.

Apply *Sonnenschein's* method (§ 134, *b*, *β*), and separate the bases from the molybdic acid in the fluid filtered off from the phospho-molybdate of ammonia. As molybdic acid comports itself with sulphuretted hydrogen and sulphide of ammonium like a metal of the sixth group, it is best to precipitate metals of the sixth and also of the fifth group from acid solutions with sulphuretted hydrogen, before proceeding to precipitate the phosphoric acid with molybdic acid; as this will leave the phosphoric acid to be separated only from the metals of the first four groups. The process is conducted as follows: mix the acid fluid, in a stoppered flask, with ammonia till it acquires an alkaline reaction, add sulphide of ammonium in sufficient excess, and digest the mixture. As soon as the solution appears of a pure yellow color, without the least tint of green, filter off the fluid, which contains sulphide of molybdenum and ammonium, wash the residue with water mixed with some sulphide of ammonium, and separate the remaining metallic sulphides and hydrated oxides of the fourth and third groups by the methods which will be found in Section V. Mix the filtrate cautiously with hydrochloric acid in moderate excess, remove the sulphide of molybdenum according to the direction of § 128, *c*, and determine the alkaline earths and alkalies in the filtrate. This method of separating the phosphoric acid from the bases is deservedly highly recommended; it is more especially suitable in cases where a small quantity of phosphoric acid has to be determined in presence of a large quantity of sesquioxide of iron. As arsenic acid and silicic acid give, with molybdic acid, similar yellow precipitates, it is necessary, if these acids are present, to remove them first. However, even if a little silico-molybdate of ammonia is mixed with the phospho-molybdate, the estimation of the phosphoric acid may yet be accurately effected (comp. § 134, *b*, γ).

As the separation of the bases from the large excess of molybdic acid used is somewhat tedious, the best way is to arrange matters so that this process may be altogether dispensed with. Supposing, for instance, you have a fluid containing sesquioxide of iron, alumina, and phosphoric acid, estimate, in one portion, by cautious precipitation with ammonia, the total amount of the three bodies; in another portion the phosphoric acid, by means of molybdic acid; and in a third, the sesquioxide of iron, by the volumetrical method (§ 113, 2, *a*). The difference gives the alumina.

§ 136.

2. BORACIC ACID.

I. *Determination.*

The determination of boracic acid is effected either in an indirect way, or in form of borofluoride of potassium.

1. The determination of the boracic acid in an aqueous or alcoholic solution cannot be effected by simply evaporating the fluid and weighing the residue, as a notable portion of the acid volatilizes and is carried off with the aqueous or alcoholic vapor. This is the case also when the solution is evaporated with oxide of lead in excess.

The best way of determining the boracic acid is therefore the following:—Mix the solution of the boracic acid with a weighed quantity of pure carbonate of soda,* varying in amount from about equal to the supposed quantity of the boracic acid present to double that amount. Evaporate the mixture to dryness, heat the residue to fusion, and weigh. The residue contains a known amount of soda, and unknown quantities of carbonic acid and boracic acid. Determine the carbonic acid by one of the methods given in § 139, and calculate the boracic acid from the difference (*H. Rose*).

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* Fused carbonate of soda answers the purpose best.

2. If boracic acid is to be determined as borofluoride of potassium, no bases except alkalies must be present. The process which succeeds best if potassa alone is present is conducted as follows:—Mix the fluid with pure solution of potassa, adding for each equivalent of boracic acid supposed to be present, at least 1 equivalent of potassa; add pure hydrofluoric acid (free from silicic acid) in excess, and evaporate, in a platinum basin, on the water-bath, to dryness. The hydrofluoric acid must be applied in sufficient quantity to let a portion of it escape in the process of evaporation, so that the *evaporating fumes* redden litmus paper. The residue consists now of K Fl, B Fl_3 and K Fl, H Fl. Treat the dry saline mass, at the common temperature, with a solution of 1 part of acetate of potassa in 4 parts of water, let it stand a few hours, with frequent stirring, then decant the fluid portion on to a weighed filter, and wash the precipitate repeatedly in the same way, and finally on the filter, with solution of acetate of potassa, until the last rinsings are no longer precipitated by chloride of calcium. By this course of proceeding, the hydrofluoride of potassium is removed, without a particle of the borofluoride of potassium being dissolved. To remove the acetate of potassa, wash the precipitate now with spirit of wine of 84° Tralles, dry at 212° F., and weigh. As chloride of potassium, nitrate and phosphate of potassa, salts of soda, and even sulphate of potassa, though the latter salt with some difficulty, dissolve in solution of acetate of potassa, the presence of these salts does not interfere with the estimation of the boracic acid; however, salts of soda must not be present in considerable proportion, as fluoride of sodium dissolves with very great difficulty. The results obtained by this method are satisfactory. *Stromeyer's* experiments gave from 97·5 to 100·7, instead of 100. For the composition and properties of borofluoride of potassium, see § 93, 5. As the salt is very likely to contain silicofluoride of barium, it is indispensable to test it first for that substance; this is done by placing a small sample of it on moist blue litmus paper, and putting another sample into cold concentrated sulphuric acid. If the blue paper turns red, and effervescence ensues in the sulphuric acid, the salt is impure, and contains silicofluoride of potassium. To remove this impurity, dissolve the remainder of the salt, after weighing it again, in boiling water, add ammonia, and evaporate, and repeat the same operation at least four times. Finally, after warming once more with ammonia, filter off the silicic acid, evaporate to dryness, and treat again with solution of acetate of potassa and alcohol (*A. Stromeyer*, "Annal. d. Chem. u. Pharm.," 100, 82). I have, however, slightly modified *Stromeyer's* method for effecting the separation of the silicic acid, the results of my experiments having convinced me that treating the salt only once with ammonia, as recommended by that chemist, is not sufficient to effect the object in view.

II. *Separation of Boracic Acid from the Bases.*

a. From the Alkalies.

Dissolve a weighed quantity of the borate in water, add an excess of hydrochloric acid, and evaporate the solution on the water-bath.

Towards the end of the operation add a few more drops of hydrochloric acid, and keep the residue on the water-bath, until no more hydrochloric acid vapors escape. Determine now the chlorine in the residue (§ 141), calculate from this the alkali, and the boracic acid from the difference.

E. Schweizer, with whom this method originated, states that it gave him very satisfactory results in his analysis of borax. It will, probably, answer also for the estimation of the bases in the case of some other borates. It is self-evident that the boracic acid may, in such cases, be estimated, in another portion of the salt, by I., 2. If you have to estimate boracic acid in presence of large proportions of alkaline salts, make the fluid alkaline with potassa, evaporate to dryness, extract the residue with alcohol and some hydrochloric acid, add solution of potassa to strongly alkaline reaction, distil off the spirit of wine, and then proceed as in I., 2 (*Aug. Stromeyer*, "Annal. d. Chem. u. Pharm.," 100, 82).

b. From almost all other Bases.

The compounds are decomposed by boiling or fusion with carbonate of potassa or hydrate of potassa; the precipitated base is filtered off, and the boracic acid determined in the filtrate, according to the directions of I., 2. If magnesia was present, a little of this is very likely to get into the filtrate; upon neutralizing with hydrofluoric acid, this separates as insoluble fluoride of magnesium, which may either be filtered off at once, or removed subsequently, by treating the borofluoride of potassium with boiling water, in which that salt is soluble, the fluoride of magnesium insoluble.

c. From the Metallic Oxides of the Fourth, Fifth, and Sixth Groups.

The metallic oxides are precipitated by sulphuretted hydrogen, or, as the case may be, sulphide of ammonium, and determined by the appropriate methods. The quantity of boracic acid may often be inferred from the loss. If it has to be estimated in the direct way, the filtrate, after addition of solution of potassa and some nitrate of potassa, is evaporated to dryness, the residue heated to redness, and the boracic acid estimated by I., 2. In cases where the metal has been precipitated by sulphuretted hydrogen from acid or neutral solutions, the boracic acid may also be determined in the filtrate, by the method given in I., 1, after being first completely freed from sulphuretted hydrogen by transmitting carbonic acid through the fluid.

d. From the whole of the Fixed Bases.

A portion of the very finely pulverized compound under examination is weighed, put into a capacious platinum crucible, and digested with a sufficient quantity of hydrofluoric acid; pure concentrated sulphuric acid is then gradually added, drop by drop, and the mixture heated, gently at first, then more strongly, until the excess of the sulphuric acid is completely expelled. In this operation the boracic acid goes off in the form of fluoride of boron ($BoO_3 + 3\,H\,Fl = B\,Fl_3 + 3\,H\,O$). The residue contains the bases in the form of sulphates; the bases are determined by the appropriate methods, and the quantity of the boracic acid is inferred from the difference between the weight of the separated base and that of the analysed borate. The application of this method presupposes, of course, that the analysed compound is decomposable by sulphuric acid.

§ 137.

3. OXALIC ACID.

I. *Determination.*

Oxalic acid is either precipitated as *oxalate of lime*, and the latter determined as *carbonate of lime;* or the amount contained in a compound is inferred from the quantity of solution of permanganate of potassa required to effect its conversion into carbonic acid; or from the quantity of gold which it reduces; or from the amount of carbonic acid which it produces upon accession of 1 equivalent of oxygen.

a. Determination as Carbonate of Lime.

Precipitate with solution of acetate of lime, added in moderate excess, and treat the precipitated oxalate of lime as directed in § 103. If this method is to yield accurate results, the solution must be neutral or made slightly acid by *acetic acid;* it must not contain alumina, sesquioxide of chromium or oxides of the heavy metals, more especially sesquioxide of iron or oxide of copper; therefore, where these conditions do not exist, they must first be supplied.

b. Determination by means of Solution of Permanganate of Potassa.

Determine the strength of the solution of permanganate of potassa, as directed § 112, 2, *a*, *cc*, by means of oxalic acid; then dissolve the compound in which the oxalic acid is to be estimated, and which must be free from all other bodies that might act on solution of permanganate of potassa, in 400 or 500 parts of water, or, as the case may be, acid and water; add, if necessary, a further, not too small, quantity of sulphuric acid, or hydrochloric acid, heat to about 140° F., and then add solution of permanganate of potassa, drop by drop, with constant stirring, until the fluid just shows a red tint (compare § 112, 2, *a*, *cc*). Knowing the quantity of oxalic acid which 100 cubic centimetres of the standard solution of permanganate of potassa will oxidize, a simple calculation will give the quantity of oxalic acid corresponding to the cubic centimetres of solution of permanganate of potassa used in the experiment. The results are very accurate (compare Experiment No. 66).

c. Determination by inference from the amount of Gold reduced by the Acid (H. Rose).

α. In Compounds soluble in Water.

Add to the solution of the oxalic acid or the oxalate a solution of sodio-terchloride, or ammonio-terchloride of gold, and digest for some time at a temperature near ebullition, with exclusion of direct solar light. Collect the precipitated gold on a filter, wash, dry, ignite, and weigh. 1 equivalent of gold (196·67) corresponds to 3 equivalents of C_2O_3 ($3 \times 36 = 108$).

β. In Compounds insoluble in Water.

Dissolve in the least possible amount of hydrochloric acid, dilute with a very large quantity of water, in a capacious flask, cleaned previously with solution of soda; add solution of gold in excess, boil the mixture some time, let the gold subside, taking care to exclude solar light, and then proceed as directed in *α*.

d. Determination as Carbonic Acid.

This may be effected either,

α. By the method of organic analysis (§ 175); or, *β*. By mixing the oxalic acid or oxalate with finely pulverized binoxide of manganese in excess, and adding sulphuric acid to the mixture, in an apparatus so constructed that the disengaged carbonic acid passes off perfectly dry.

The theory of this method may be illustrated by the following equation:

$$C_2O_3 + Mn\,O_2 + S\,O_3 = Mn\,O,\,S\,O_3 + 2\,C\,O_2$$

For each equivalent of oxalic acid we obtain accordingly 2 equivalents of carbonic acid. For the apparatus and process, I refer to the chapter on the examination of manganese ores, in the special part of this work. Here I may remark that free oxalic acid must first be prepared for the process by slight supersaturation with ammonia, and also that 9 parts of anhydrous oxalic acid require theoretically 11 parts of pure binoxide of manganese. Since an excess of the latter substance does not interfere with the accuracy of the results, it is easy to determine the amount to be added. The binoxide of manganese need not be pure, provided it contains no carbonate. This method is very expeditious, and gives accurate results, if the process is conducted in an apparatus sufficiently light to admit of the use of a delicate balance.

Instead of binoxide of manganese, chromate of potassa may be used; compare § 130, *c*.

II. *Separation of Oxalic Acid from the Bases.*

The most convenient way of analysing oxalates is, in all cases, to determine in one portion, the acid, by one of the methods given in I., in another portion, the base, particularly as the latter object may be effected by simple ignition in the air, which reduces the salt either to the metallic state (*e.g.*, oxalate of silver), or to pure oxide (*e.g.*, oxalate of lead), or to carbonate (*e.g.*, the oxalates of the alkalies and alkaline earths).

If acid and base have to be determined in one and the same portion of the oxalate, the following methods may be resorted to:

a. The oxalic acid is determined by I., *c*, and the gold separated from the bases in the filtrate by the methods given in Section V.

b. In many soluble salts the oxalic acid may be determined by the method I., *a*; separating the bases afterwards from the excess of the salt of lime by the methods given in Section V.

c. All oxalates whose bases are precipitated by carbonate of potassa or carbonate of soda, and are insoluble in an excess of the precipitant, may be decomposed by boiling with an excess of solution of carbonate of potassa or carbonate of soda, into oxide or carbonate on the one, and alkaline oxalate on the other side.

d. All salts of oxalic acid with the oxides of the fourth, fifth, and sixth groups may be decomposed with sulphuretted hydrogen, or with sulphide of ammonium.

§ 138.

4. HYDROFLUORIC ACID.

I. *Determination.*

Free hydrofluoric acid in aqueous solution is best determined as *fluoride of calcium*. For this purpose, carbonate of soda is added in moderate excess, then a solution of chloride of calcium as long as a precipitate continues to form; when the precipitate, which consists of fluoride of calcium and carbonate of lime, has subsided, it is washed, first by decantation, afterwards on the filter, and dried; when dry, it is ignited in a platinum crucible (§ 53); water is then poured over it, in a platinum or porcelain dish, acetic acid added in slight excess, the mixture evaporated to dryness on the water-bath, and heated on the latter until all odor of acetic acid disappears. The residue, which consists of fluoride of calcium and acetate of lime, is treated with water, the fluoride of calcium filtered off, washed, dried, ignited (§ 53), and weighed. If the precipitate of fluoride of calcium and carbonate of lime were treated with acetic acid, without previous ignition, the washing of the fluoride would prove a difficult operation. Presence of nitric or hydrochloric acid in the aqueous solution of the hydrofluoric acid does not interfere with the process (*H. Rose*).

II. *Separation of Fluorine from the Metals.*

a. Soluble Fluorides.

If the solutions have an acid reaction, carbonate of soda is added in excess. If this produces no precipitate, the fluorine is determined by the method given in I., and the bases in the filtrate are separated from the excess of lime, and from the soda, by the methods given in Section V. But if the carbonate of soda produces a precipitate, the mixture is heated to boiling, then filtered, and the fluorine determined in the filtrate by the method given in I., the base is in the residue, which must, however, first be tested, to make sure that it contains no fluorine. Neutral solutions are mixed with a sufficient quantity of chloride of calcium, and the mixture heated to boiling, in a platinum dish or, but less appropriately, in a porcelain dish; the precipitate of fluoride of calcium is allowed to subside, thoroughly washed with hot water, by decantation, transferred to the filter, dried, ignited, and weighed. The bases in the filtrate are then separated from the excess of the salt of lime by the usual methods. That the bases may be determined also in separate portions by the methods given in *b*, need hardly be stated.

b. Insoluble Fluorides.

α. Anhydrous insoluble Fluorides.

The finely pulverized and accurately weighed substance under examination is heated for some time with concentrated pure sulphuric acid, and the residue finally ignited until the free sulphuric acid is completely expelled. The residuary sulphate is weighed, and the metal contained in it calculated. The difference between the calculated weight of the metal and that of the original fluoride shows the amount of fluorine originally present in the analysed compound. In cases where we have to deal with metals whose sulphate gives off part of the sulphuric acid upon ignition, or where the residue contains several metals, it is necessary to subject the residue to a further analysis before this calculation can be made.

β. Hydrated insoluble Fluorides.

A sample of the compound under examination is heated in a tube.

aa. The Water expelled is perfectly neutral to Litmus Paper.

In this case the amount of water present is ascertained by igniting the hydrated compound, and the fluorine and metal are subsequently determined as directed in II., *b*, *a*.

bb. The Water expelled has an acid reaction.

The fluoride under examination is, in the first place, treated with sulphuric acid as directed in II., *b*, *a*, to determine the metal on the one hand, and the water + fluorine on the other. Another weighed portion is then mixed, in a small retort, with about 6 parts of recently ignited oxide of lead; the mixture is covered with a layer of oxide of lead, the retort weighed, and the water (which is now entirely free from admixture of hydrofluoric acid) expelled by the application of heat, increased gradually to redness. The weight of the expelled water is inferred from the loss. The first operation having given us the exact amount of water + fluorine, the quantity of the latter substance may now be readily calculated, by simply subtracting from the combined weight of the water + fluorine, the weight of the water expelled in the second operation.

In the fifth section we shall have occasion to speak of another method of determining fluorine (in the chapter on the separation of fluorine from silicic acid).

Fourth Division of the First Group of the Acids.

CARBONIC ACID—SILICIC ACID.

§ 139.

1. CARBONIC ACID.

I. *Determination.*

a. In a mixture of Gases.

Measure the gases accurately, in a graduated tube over mercury, insert into the tube a moistened ball of hydrate of potassa, cast on a platinum wire in a pistol bullet-mould, and leave this in the tube for 24 hours, or until the volume of the gas ceases to show further diminution; withdraw the ball, and measure the gas remaining; the amount of carbonic acid gas originally present is inferred from the difference, provided the gaseous mixture contained no other gas liable to absorption by potassa (compare also, §§ 13–16).

b. In Aqueous Solution.

a. Mix solution of chloride of barium or chloride of calcium* with solution of ammonia in excess, heat the mixture to boiling, let the precipitate deposit, and then filter. Have ready several flasks of about 300 cubic centimetres capacity each, provided with tight-fitting corks, and pour into each about 50 c.c. of the filtrate. The method to be adopted for adding, without loss of gas, certain definite quantities of solution of carbonic acid to the filtrate in the flasks, depends upon whether the carbonic acid water is contained in a stone bottle, or flowing from a pipe, or whether it can be taken directly from the spring. In the former case weigh the flasks, with the ammoniacal chloride of barium solution in them, separately, together with the cork; then let the water run into each flask, with proper care, until nearly full,† cork instantly, and weigh again; this will give the exact quantity of water contained in each flask. Or, pour into each flask, in the first instance, *exactly* 50 cubic centimetres of the ammoniacal solution of chloride of barium, or chloride of calcium, then fill in the water, in the way just stated, mark with a diamond, or by means of a small paper slip pasted on the outside of the flask the point to which it reaches; measure afterwards the contents of the flask up to the mark, and deduct the 50 cubic centimetres of chloride of barium or chloride of calcium solution, when the difference will show the quantity of carbonic acid water added.

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* Solution of chloride of barium is preferable in cases where the after process is to be conducted according to *aa*; solution of chloride of calcium in cases where *bb* to be resorted to.

† If the carbonic acid water is in a stone bottle, it should always be transferred to the flask by means of a siphon, after being cooled first to about 39·2° F. If the water were poured in direct from the bottle, some carbonic acid gas might also find its way into the flask, together with the water.

In the latter case, where the water can be taken direct from the spring, you will find the estimation of the volume more convenient by making use of a siphon or large pipette, dipped into the spring, so that the water enters through the lower orifice. The siphon or pipette used for the purpose must have a mark cut in the glass a little below the upper orifice; the exact volume which it holds up to this mark may be determined either before or after the operation, by filling it with water up to the mark, and measuring in a graduated glass. When the siphon or pipette is quite full, lift it out of the spring, wipe the outside dry, with proper expedition; let some water flow out, until the contents reach just up to the mark; then empty into one of the flasks containing the ammoniacal solution of chloride of barium, or chloride of calcium, and cork instantly. Proceed in the same way with the other flasks. The ammoniacal chloride of barium or chloride of calcium solution in the flasks generally turns turbid as soon as the carbonic acid water is poured in; but, it is only after standing some time on the water bath, or even after actual ebullition, that the whole of the carbonic acid separates in form of carbonate of baryta or carbonate of lime.[*] When this point has been attained, allow the precipitate to subside, with exclusion of air, and then proceed by one of the following methods :—

aa. Estimation of the Carbonic Acid by the Gravimetrical Method.

Decant the supernatant fluid rapidly on to a filter, secluded as much as possible from access of air; fill the flask with warm water, and insert the cork; shake, let the solid particles deposit, decant again, and repeat this washing by decantation once more; transfer the precipitate now to the filter, wash until the last rinsings remain clear upon addition of solution of nitrate of silver, dry, ignite gently, and weigh (§ 101, 2, *a*). The amount of the carbonic acid may now be calculated from the weight of the carbonate of baryta, provided the analysed solution contained, besides carbonic acid, no other substance liable to be precipitated by ammonia and chloride of barium. But should the latter be the case, and the precipitated carbonate of baryta contain an admixture of carbonate of lime, phosphate of baryta, sesquioxide of iron, or other similar substances, the carbonic acid must be determined in the gently ignited, but not weighed precipitate, as directed in II., *d*. The filter, freed as completely as possible from adhering matter, should be incinerated, and the ashes added to the precipitate. If the quantity of the precipitate is very large, it is best first to weigh the whole of it, and then to determine the carbonic acid in a weighed portion of the uniformly mixed powder.

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[*] The tardiness of this reaction is explained, as is well known, upon the assumption that carbonic acid and ammonia, coming in contact, form, in the first place, carbamate of ammonia, $CO_2 + 2NH_3 = C\left\{\begin{matrix}C\\NH_2,\end{matrix}\right.NH_4O$.

If the last particles of the precipitate cannot be removed from the flask by mechanical means, they are dissolved in a little dilute hydrochloric acid (the glass having previously been thoroughly washed), the solution is precipitated with carbonate of soda, and the trifling precipitate formed filtered off on a separate small filter, which is incinerated with the larger one.

bb. Estimation of the Carbonic Acid by the Volumetrical Method.

Filter as in *aa*; there is no necessity, however, to collect the whole of the precipitate on the filter, as the last particles adhering to the inside of the flask may be left and washed by decantation. Put the funnel with the filter containing the precipitate on the flask in which the precipitation has been effected, make a small hole in the point of the filter, and rinse the thoroughly washed precipitate into the flask, with the aid of a washing bottle. Dry the filter, incinerate, and add the ash to the precipitate in the flask. Add now a little tincture of litmus, and then, from a *Mohr's* burette (see § 21), standard (or, according to circumstances, decimal standard) nitric or hydrochloric acid, until the fluid shows a distinct red color; expel the carbonic acid by heat, and then add solution of soda of known strength until the fluid just appears blue. After noting the number of cubic centimetres of the acid and soda, add again about 1 cubic centimetre of acid, and, after heating to boiling, solution of soda until the fluid again just appears blue. This operation may be repeated several times. By subtracting the volume of acid corresponding to the volume of solution of soda used in the process from the entire volume of acid added in the several experiments, you find the quantity of acid which has served to expel from the carbonate of baryta the carbonic acid, and is accordingly equivalent to the latter. For the details of this expeditious and very accurate method, see § 223. As the coloring matter of the litmus is sometimes thrown down, along with silicic acid separating from the precipitate, it is occasionally found necessary to add again some tincture of litmus. If this should fail to lead to the desired result, solution of soda is added until the reaction is almost complete; the amount of the soda solution left in the burette is then read off, the fluid diluted to a certain definite volume, and filtered; one-half the volume taken of the clear filtrate and solution of soda very cautiously added until the fluid appears blue; the quantity of soda solution required to effect this purpose is then doubled, and the result added to the quantity first used.

β. In cases where rigorously accurate results are not required, and it is simply wished to ascertain approximately and comparatively the amount of free carbonic acid in a mineral water, *R. Kersting's* method ("Annal. d. Chem. u. Pharm.," 94, 112,) may be resorted to. This method is based upon the fact that tincture of litmus is colored violet by free carbonic acid, but not by bicarbonate of soda. If, therefore, to a solution of carbonate of soda, colored blue by litmus, dilute sulphuric acid is cautiously added, the fluid will acquire a violet tint as soon as NaO, SO_3 and $NaO, 2CO_2$ have been formed in it, and another drop of sulphuric acid is added, which disengages some carbonic acid. The experiment requires, *a*, standard solution of dilute sulphuric acid, containing in 1 cubic centimetre 10 milligrammes of SO_3, corresponding to 11 milligrammes of carbonic acid; this is prepared by mixing 1 volume of standard sulphuric acid (§ 215) with 3 volumes of water; *b*, a concentrated solution of soda containing some carbonic acid, as is, moreover, usually the case.

aa. Add to about 450 cubic cent. of pure water 1½ cub. cent. of tincture of litmus, prepared by digesting in the cold equal parts of litmus and water; add exactly 5 c.c. of the solution of soda, dilute with water to 500 c.c. of fluid; take out, by means of the pipette, 3 several portions of 100 c.c. each, pour them respectively into 3 beakers, standing on a white ground, and add to each successively, with proper care, dilute standard sulphuric acid, until the color appears distinctly violet. The experiment must be made in the daytime, and by a good light; towards the termination of the process, you must always wait 1 or 2 minutes after each addition of acid, to allow the change of color to become distinctly visible. Bestow increased care and attention upon the experiment with the fluid in the second beaker, and in the third. Multiply by 5 the volume of acid used in the most accurate of the three experiments, and mark the result as the quantity of acid corresponding to 5 c.c. of the concentrated solution of soda.

bb. Add to about 450 to 500 cubic centimetres of the carbonic acid water under examination, carefully measured, either before the experiment or after, 5 c.c. of the soda solution *b*,* and mix. Of this mixture, which is generally turbid, owing to the separation of carbonates of alkaline earths, take out successively 3 several portions of 100 c.c. each, add to each portion 4 drops of litmus tincture, and then, cautiously and with stirring, sulphuric acid, until the fluid shows a violet tint. Bestow increased care and attention upon the experiment with the second portion and with the third. By determining now the quantity of carbonic acid water used, if you have not done so before, you find the last factor still required for calculating the results.

Suppose the experiment has been made with 455 c.c. of mineral water, and you have added to this 5 c.c. of solution of soda; 100 c.c. of your mixture required 6 c.c. of sulphuric acid; 460 c.c. would, accordingly, have required 27·5 c.c. Now suppose 5 c.c. of soda solution have required 90·6 c.c. of acid, the 455 c.c. of the carbonic acid water contained, accordingly, as much free carbonic acid as corresponds to 90·6 − 27·6 = 63 c.c. of sulphuric acid, that is to say, 63 × 0·011 = 0·693 grammes; as for every 2 equivalents of carbonic acid, which are ultimately present in the fluid in the state of bicarbonate of soda, there is required 1 equivalent less of sulphuric acid; 1 equivalent of $SO_3 = 40$ corresponds, consequently, to 2 equivalents of $CO_2 = 44$, or 10 milligrammes SO_3 (*i.e.* the quantity contained in 1 c.c.) correspond to 11 milligrammes CO_2.

To obtain properly corresponding results by this method requires a practised eye; the method has, therefore, rather a subjective than an objective value; and, in my opinion, ought never to be employed in cases intended for publication.

II. *Separation of Carbonic Acid from the Bases, and its estimation in Carbonates.*

a. Separation from Alkalies.

aa. If the salts contain 1 equivalent of carbonic acid to 1 equivalent of base, and there is no other salt with alkaline reaction present, the most convenient way is to determine the quantity of the base by the alkalimetrical method (§§ 219, 220), and to calculate for each equivalent of base 1 equivalent of carbonic acid.

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* If the water is in a bottle, cool it down to about 39·2° F., then remove the stopper, take out a little of the water, and instantly add the solution of soda. If 5 c.c. is not sufficient to make the water alkaline, add 10 c.c.

bb. If the salt contains more than 1 equivalent of carbonic acid to 1 equivalent of base, mix the solution of a weighed portion with a mixture of chloride of barium, or chloride of calcium and ammonia, heated to boiling and filtered, and proceed exactly as directed in I., *b, a.*

cc. If the salts contain less than 1 equivalent of carbonic acid to 1 equivalent of base, mix the dilute solution of a weighed portion with an excess of pure and neutral solution of chloride of barium or chloride of calcium; heat, let deposit, and treat the washed precipitate as in I., *b, a, aa,* or *bb.*

b. From the Alkaline Earths.

If the compounds are neutral and contain no other acids forming with the alkalies salts with alkaline reaction, the bases in them may be determined by the alkalimetrical method (§ 223), and 1 equivalent of carbonic acid reckoned for each equivalent of base.

c. Separation of Carbonic Acid from Bases which upon Ignition readily and completely yield the Carbonic Acid with which they are combined.

Such are, for instance, the carbonates of the oxides of zinc, cadmium, lead, copper, magnesium, &c.

a. Anhydrous Carbonates.

Heat the weighed substance, in a platinum crucible (carbonates of cadmium and lead in a porcelain crucible), to ignition, and keep in that state until the weight of the residue remains constant. The results are, of course, very accurate. Substances liable to absorb oxygen upon ignition in the air are ignited in a bulb-tube, through which a stream of dry carbonic acid gas is conducted during the process. The carbonic acid is inferred from the loss.

β. Hydrated Carbonates.

The substance is ignited in a bulb-tube through which dried air or, in presence of oxidizable substances, carbonic acid is transmitted, and which is connected with a chloride of calcium tube, by means of a dry, close-fitting cork. During the ignition, the posterior end of the tube is, by means of a small lamp, kept sufficiently hot to prevent the condensation of water in it, care being taken, however, to guard against burning the cork. The loss of weight of the tube gives the amount of the water + the carbonic acid; the increase of weight gained by the chloride of calcium tubes gives the amount of the water, and the difference accordingly that of the carbonic acid. A somewhat wide glass tube may also be substituted for the bulb tube, and the substance introduced into it in a little boat, which is weighed before and after the operation.

d. Separation of Carbonic Acid from all Bases without exception, in Anhydrous Carbonates.

The carbonate under examination is weighed in a platinum crucible, and about 4 times its weight of fused biborate of soda (§ 64, 6) added, which has been heated again just previous to weighing. The mixture is weighed, and heat is then applied, which is gradually increased to intense ignition, and maintained at this temperature until the contents of the crucible are in a state of calm fusion. The crucible is now allowed to cool, and, when cold, weighed. The loss of weight indicates the amount of carbonic acid originally present in the ignited compound. The results are very accurate (*Schaffgottsch*).

e. From all Bases without exception, no matter whether the Compounds are anhydrous or not.

a. Estimation of the Acid from the loss of weight.

aa. Carbonates whose Bases form Soluble Salts with Sulphuric Acid. The process is conducted in the apparatus illustrated by Fig. 66.

The size of the flasks depends upon the capacity of the balance which the operator possesses. The tube *a* is closed at *b* by means of a small wax stopper;* the other end of the tube *a* is open, as are also both ends of *c* and *d*. The flask B is nearly half filled with concentrated sulphuric acid; the tubes *a*, *c*, and *d*, must fit air-tight in the perforations of the corks, and the latter equally so in the mouths of A and B. A weighed portion of the carbonate under examination is put into A; this flask is then filled about one-third with water, the cork properly inserted, and the apparatus placed in equilibrium upon the balance.

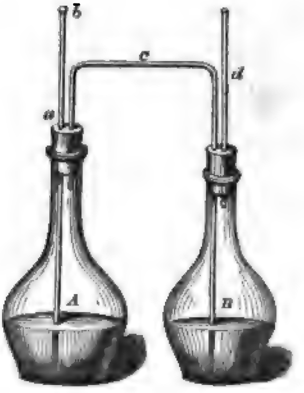

Fig. 66.

A few bubbles of air are now sucked out of *d*, by means of a small india-rubber tube. This serves to rarefy the air in A also, and causes the sulphuric acid in B to ascend in the tube *c*. The latter is watched for some time, to ascertain whether the column of sulphuric acid in it remains stationary, which is a proof that the apparatus is air-tight. Air is then again sucked out of *d*, which causes a portion of the sulphuric acid to flow over into A. The carbonate in the latter flask is decomposed by the sulphuric acid, and the liberated carbonic acid, completely dried in its passage through the concentrated sulphuric acid in B, escapes through *d*. When the evolution of the gas slackens a fresh portion of sulphuric acid is made to pass over into A, by renewed suction through *d*; and the same operation is repeated until the whole of the carbonate is decomposed. A more vigorous suction is now applied, to make a larger amount of sulphuric acid pass over into A, whereby the contents of that flask are considerably heated; when the evolution of gas bubbles has completely ceased, the wax stopper on *a* is opened, or the glass rod removed from the india-rubber cap, and suction applied to *d*, until the air sucked out tastes no longer of carbonic acid.†

The apparatus is allowed to cool and then replaced upon the balance, and the equilibrium restored by additional weights. The sum of the weights so added indicates the amount of carbonic acid originally present in the analysed compound.

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* Or with a small piece of india-rubber tube, drawn over it, and having inserted in the other end a short piece of glass rod.

† In accurate experiments, it is advisable to connect the end *b* of the tube *a* with a chloride of calcium tube during the process of suction.

If the flasks A and B are selected of small size, the apparatus may be so constructed that, together with the contents, it need not weigh above seventy grammes, admitting thus of being weighed on a delicate balance. The results obtained by the use of this apparatus, first suggested by *Will* and *Fresenius*, are very accurate, provided the quantity of the carbonic acid be not too trifling. I have not yet been able to convince myself that any of the proposed modifications of this apparatus affords essential advantages.

For the mode of proceeding in cases where the carbonate is mixed with a metallic sulphide or chloride, I refer to Section V.

bb. Carbonates whose Bases form insoluble Salts with Sulphuric Acid.

The analysis of such carbonates cannot well be effected by the method *aa*, as the insoluble sulphate formed (sulphate of lime, for instance) partially protects the yet undecomposed portion of the carbonate from decomposition. The apparatus is therefore modified as shown in Fig. 67.

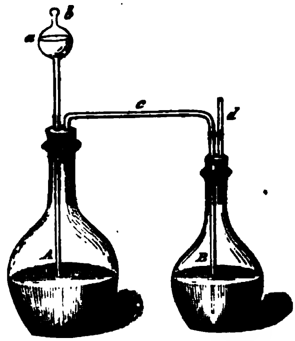

Fig. 67.

It will be seen from the engraving that the modification consists simply in the tube *a*, *b*, being expanded at the upper end into a bulb, and drawn out to a fine point at the lower end.

The process is conducted as follows: A weighed portion of the carbonate is put into A, which flask is filled about one-third with water. The bulb-tube *a* contains an amount of dilute nitric acid, more than sufficient for the decomposition of the carbonate, and which is prevented from flowing through the narrow aperture of this tube by the little wax stopper *b*.[*] The point of this tube must not dip into the water in A. The apparatus, having been put in equilibrium on the balance, the tube *a* is carefully and cautiously moved down, until its point nearly touches the bottom of A. The wax stopper *b* is then momentarily raised, or the glass rod removed from the india-rubber cap, so as to allow a small quantity of nitric acid to flow out of tube *a*; and the same operation is repeated, until the carbonate is completely decomposed. A is then heated to from 176° to 194° F., the wax stopper (or india-rubber cap) opened a little, and suction applied to the tube *d*, until the air tastes no longer of carbonic acid. The diminution of weight is ascertained when the apparatus is completely cooled.

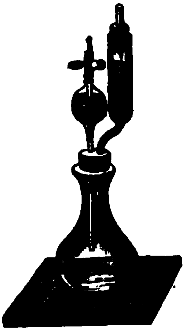

Fig. 68.

It will be seen at a glance that a different construction may also be given to the apparatus; that, for instance, the tube *a* may be connected, instead of with B, with a chloride of calcium tube, or with a tube filled with pumice stone or asbestos moistened with sulphuric acid; also, that the substance to be analysed may be put into a small tube, which stands upright at first, or suspended from a thread, but subsequently, after weighing the apparatus, upset or lowered into the dilute acid in the flask; also, that the closing of *a* may be effected by means of an india-rubber connector with compression clamp, &c. Such modifications, if they are judicious, do not alter the accuracy of the results. Fig. 68 shows an apparatus modified in this manner, by *Fr. Mohr.*

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[*] Or india-rubber cup, with glass rod. See *aa*.

The apparatus proposed by *Geissler* ("Journ. f. prakt. Chemie," 60, 35) is one of the most convenient (see Fig. 69).

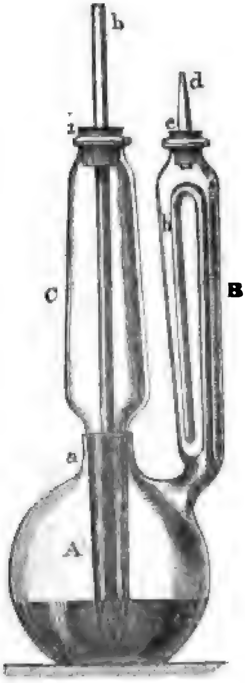

Fig. 69.

The apparatus consists of two parts, A B and C. C is ground into the neck of A (a), so as to close air-tight, and yet admit of being readily removed, for the purpose of filling and emptying A. b c is a glass tube, open at both ends, and ground water-tight into C, at the lower end (c); it is kept in the proper position by means of a movable cork, i. The illustration shows the construction of the apparatus in other respects. The cork e must close air-tight, as must the tube d in the cork. The weighed substance to be decomposed is put into A, water added to the extent indicated in the engraving, and the substance shaken towards the side of the flask. C is now filled nearly to the top with dilute nitric acid, with the aid of a pipette, after having previously turned the cork i upwards, without raising b; the cork is then again turned down, and C inserted into A; B is filled somewhat more than half with concentrated sulphuric acid, and b closed at the top with a little wax stopper, or a piece of india-rubber tube, with a small glass rod inserted in it. After weighing the apparatus, the decomposition is effected by raising b a little, and thus causing acid to pass from C into A. The carbonic acid escapes through h into the sulphuric acid, where it is dried; it then leaves the apparatus through d. After the decomposition has been effected, A is gently heated, the little wax stopper on b opened, and the carbonic acid still remaining in the apparatus sucked out through d, by means of a small india-rubber tube. The apparatus is finally weighed when cold.*

β. Determination of the Acid by expulsion and conversion into Carbonate of Lime or Carbonate of Baryta.

Expel the carbonic acid by a stronger acid, and conduct the expelled acid into a solution of chloride of calcium, or chloride of barium, mixed with ammonia, or into a solution of ammonia, to which chloride of calcium, or chloride of barium is afterwards added. Determine the carbonic acid in the carbonate of lime or baryta formed, as in I., *b.*

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* Several other forms of this apparatus have been proposed by *H. Rose*, *Fritsche*, *Rogers* (see *H. Rose's* "Manual of Analytical Chemistry," ii. 806); *Vohl* ("Annal. d. Chem. u. Pharm.," 66, 247); *M. Schaffner* ("Annal. d. Chem. u. Pharm.," 82, 335); *Werther* (Modification of *Geissler's* apparatus—"Journ. f. prakt. Chem.," 61, 99); *J. D. Smith* ("Chem. Gaz.," 1855, 201); *A. Mayer* ("Journ. f. prakt. Chem.," 67, 63); *Th. Simmler* ("Journ. f. prakt. Chem.," 71, 158); *Al. Bauer* (private communication), and others.

The construction of proper apparatus for the expulsion of carbonic acid and its subsequent absorption, offers a wide field to the ingenuity of inventors. However, the apparatus constructed by *Fr. Mohr* answers the purpose very well (see Fig. 70).

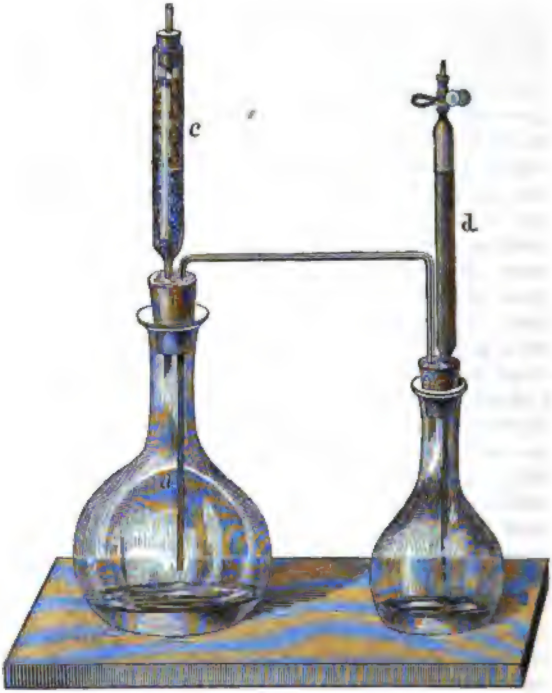

Fig. 70.

b contains the weighed substance, some water, and a little tincture of litmus; *d*, hydrochloric acid. The flask *a* is filled about $\frac{1}{8}$ with ammonia quite free from carbonic acid,* the liquid being poured in through the tube *c*, which contains coarse fragments of glass. The two flasks are united by a connecting tube bent twice at right angles. The limb in *a* does not reach sufficiently low down to dip into the ammonia. When everything is properly prepared, and the operator has convinced himself that the apparatus is perfectly tight, the clamp which closes the caoutchouc connector at the top of *d* is opened, so as to allow acid to flow out from *d*, until the fluid in *b* looks intensely red. The contents of *b* are then heated to boiling. After this, the source of heat is removed to allow *b* to fill again with air; the contents of *b* are again heated to boiling, and the same operation repeated several times. This serves to force every trace of carbonic acid from *b* into *a*. It is advisable, in this operation, to warm the ammonia in *a*, so as to fill the empty part of the flask with ammoniacal gas. When the apparatus is quite cold, the flask *b* is removed, and the perforated cork taken out of the tube *c*. The fragments of glass in the latter are thoroughly rinsed with distilled water boiled free from air, as also the limb of the connecting tube in *a*, the rinsings of course flowing into the flask *a*. A sufficient quantity of solution of chloride of calcium is now added to the fluid in *a*, the mixture heated to boiling, filtered, and the further process conducted as in I., *b*, *a*, *bb*.

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* The ammonia must remain clear when mixed with chloride of calcium and heated to boiling.

Fr. Mohr obtained very accurate results by this method.

§ 140.

2. Silicic Acid.

I. *Determination.*

The direct estimation of silicic acid is invariably effected by converting the soluble modification of the acid into the insoluble modification, which is effected by evaporating and heating; the insoluble modification is then, after removal of all foreign matter, ignited and weighed.

For the guidance of the student I would observe here that, to guard against mistakes, he should always *test the purity of the weighed silicic acid.* The methods of testing will be found below.

If you have free silicic acid in the state of hydrate, in an aqueous or acid solution free from other fixed bodies, simply evaporate the solution in a platinum dish, ignite and weigh the residue.

II. *Separation of Silicic Acid from the Bases.*

a. In all Compounds which are decomposed by Hydrochloric or Nitric Acid.

To this class belong the silicates soluble in water, as well as many of the insoluble silicates, as, for instance, nearly all zeolites.

The compound under examination is very finely pulverized, the powder dried at a temperature not exceeding 212° F., and put into a platinum or porcelain dish (in the case of silicates whose solution might be attended with disengagement of chlorine, platinum cannot be used); a little water is then added, and the powder mixed to a uniform paste. Moderately concentrated hydrochloric acid, or, if the substance contains lead or silver, nitric acid, is now added, and the mixture digested at a very gentle heat, with constant stirring, until the substance is completely decomposed, in other terms until the glass rod, which is rounded at the end, encounters no more gritty powder, and the stirring proceeds smoothly without the least grating.

The silicates of this class do not all comport themselves in the same manner in this process, but show some differences; thus most of them form a bulky gelatinous mass, whilst in the case of others the silicic acid separates as a light pulverulent precipitate; again, many of them are decomposed readily and rapidly, whilst others require protracted digestion.

When the decomposition is effected, the mixture is evaporated to dryness on the water-bath, and the residue heated, with frequent stirring, until all the small lumps have crumbled to pieces, and the whole mass is thoroughly dry, and until no more acid fumes escape. It is always the *safest* way to conduct the operation of drying on the water-bath.

In cases where it appears desirable to accelerate the desiccation by the application of a stronger heat, an air-bath may be had recourse to; which may be constructed in a simple way, by suspending, by wire hooks, the dish containing the substance, in a somewhat larger dish of silver or iron, in a manner to leave everywhere between the two dishes a small space of uniform width. Direct heating over the lamp is not advisable, as in the most strongly heated parts the silicic acid is liable to unite again with the separated bases to compounds which are not decomposed, or only imperfectly, by hydrochloric acid.

When the mass is cold, it is brought to a state of semi-fluidity by thoroughly moistening it with hydrochloric acid; after which it is allowed to stand for half an hour, without heating; it is then diluted with hot water, stirred, allowed to deposit, and the fluid decanted on to a filter; the residuary silicic acid is again treated with hot water, the mixture stirred, allowed to deposit, and the fluid once more decanted; after a third repetition of the same operation, the precipitate also is transferred to the filter, thoroughly washed with hot water, well dried, and at last strongly ignited, as directed in § 52 or in § 53. For the properties of the residue, see § 93, 9. The results are accurate. The bases, which are in the filtrate as chlorides, are determined respectively by the appropriate methods. Deviations from the instructions here given are likely to entail loss of substance; thus, for instance, if the mass is not *thoroughly* dried, a not inconsiderable portion of the silicic acid passes into the solution, whereas, if the instructions are strictly complied with, only traces of the acid are dissolved; in accurate analyses, however, even such minute traces must not be neglected, but should be separated from the bases precipitated from the solution. This separation may be readily effected by dissolving the precipitated bases, after ignition and weighing, in hydrochloric or sulphuric acid, with the aid of heat; the minute portion of silicic acid which has passed into the solution, and has been thrown down with the bases, is left undissolved. Again, if the silicic acid is not *thoroughly* dried previous to ignition, the aqueous vapor disengaged upon the rapid application of a strong heat may carry away particles of the light and loose silica.

The *purity* of the silicic acid* is tested best in the following manner:—heat a moderately concentrated solution of pure carbonate of soda to boiling, in a silver or platinum dish, or in a porcelain dish, and add a small quantity of the silicic acid. If it dissolves completely, this is a proof of its purity; but if it leaves a residue, the remainder of the silicic acid must be weighed, and the substance or substances which it contains in admixture determined as directed in *b*, and the result, of course, calculated upon the whole amount analysed.

If you have pure hydrofluoric acid, you may also test the purity of the silicic acid in a very easy manner, by pouring this acid over it, in a platinum dish; upon the evaporation of the solution, the silicic acid, if *pure*, will volatilize completely (as fluoride of silicon). If a residue remains, moisten this once more with hydrofluoric acid, add a few drops of sulphuric acid, evaporate, and ignite; the residue consists of the sulphates of the bases which the silicic acid contained in admixture (*Berzelius*).

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* This testing is more especially necessary in cases where the silicic acid has separated, not in the gelatinous state, but in the pulverulent form.

b. Compounds which are not decomposed by Hydrochloric Acid or Nitric Acid.

a. Decomposition and Solution by Fusion with Carbonated Alkali.

Reduce the substance under examination to an impalpable powder, by trituration and sifting (§ 25); transfer to a platinum crucible, and mix with about 4 times the weight of pure anhydrous carbonate of soda or carbonate of soda and potassa, with the aid of a rounded glass rod; wipe the rod against a small portion of carbonate of soda on a card, and transfer this also from the card to the crucible. Cover the latter well, and heat, according to size, over a gas- or spirit-lamp with double draught, or in a blast gas-lamp; or, insert in a Hessian crucible, compactly filled up with calcined magnesia, and heat in a charcoal fire.

Apply at first a moderate heat, to make the mass simply agglutinate; the carbonic acid will, in that case, escape from the porous mass, with ease and without spurting. Increase the heat afterwards, finally to a very high degree, and terminate the operation only when the mass appears in a state of calm fusion, and gives no more bubbles.

The platinum crucible in which the mass is fused must not be too small; in fact, the mixture should only half fill it. The larger the crucible, the less risk of loss of substance. As it is of importance to watch the progress of the operation, the lid must be easily removable; a simple concave cover, loosely put on, is therefore preferable to an overlapping lid. If the process is conducted over the spirit- or simple gas-lamp, a mixture of carbonate of soda and carbonate of potassa is preferable to carbonate of soda, as it fuses much more readily than the latter. In heating over a lamp, the crucible should always be supported on a triangle of platinum wire (see Fig. 57), with the opening just sufficiently wide to allow the crucible to drop into it fully one-third, yet to retain it firmly, even with the wire at an intense red heat. When conducting the process over a spirit-lamp with double draught, or over a simple gas-lamp, it is also advisable, towards the end of the operation, when the heat is to be raised to the highest degree, to put a chimney over the crucible, with the lower border resting on the ends of the iron triangle which supports the platinum triangle; this chimney should be about 12 or 14 centimetres high, and the upper opening measure about 4 centimetres in diameter.

When the fusion is fully effected, the red-hot crucible is removed with pincers, and placed on a cold, thick, clean, iron plate, or marble slab, on which it will rapidly cool; it is then generally easy to detach the fused cake in one piece.

The cake (or, under certain circumstances, the crucible with its contents) is put into a beaker, from 10 to 15 times the quantity of water poured over it, and hydrochloric acid gradually added, or, under certain circumstances, nitric acid; the beaker is covered with a glass plate, or, which is much better, with a large watch-glass or porcelain dish, perfectly clean outside, to prevent the loss of the drops of fluid which the escaping carbonic acid carries along with it; the drops thus intercepted by the cover are afterwards rinsed into the beaker. The crucible is also rinsed with dilute hydrochloric acid, and the solution obtained added to the fluid in the beaker.

The solution is promoted by the application of a gentle heat, which is continued for some time after, to ensure the complete expulsion of the carbonic acid; since otherwise some loss of substance might be incurred, in the subsequent process of evaporation, by spurting caused by the escape of that acid.

If in the process of treating the fused mass with hydrochloric acid, a powder subsides (chloride of sodium or chloride of potassium), this is a sign that more water is required.

If the decomposition of the mineral has succeeded to the full extent, the hydrochloric acid solution is either perfectly clear, or light flakes of silicic acid only are floating in it. But if a heavy powder subsides, which feels gritty under the glass rod, this consists of undecomposed mineral. The cause of such imperfect decomposition is generally to be ascribed to imperfect pulverization.

In such cases the undecomposed portion may be fused once more with carbonated alkali; the better way, however, is to repeat the process with more finely pulverized mineral.

The hydrochloric or nitric acid solution obtained is poured, together with the silicic acid floating in it, into a porcelain or, better, into a platinum dish, and treated as directed in § 140, II., *a.*

That the fluid may not be too much diluted, the beaker should not be rinsed, or only once, and the few remaining drops of solution dried in it; the trifling residue thus obtained is treated in the same way as the residue left in the evaporating basin.

This is the method most commonly employed to effect the decomposition of silicates insoluble in acids; that it cannot be used to determine alkalies in silicates is self-evident.

β. Decomposition and Solution by means of Hydrofluoric Acid.

aa. By Hydrated Hydrofluoric Acid.

The finely-pulverized silicate is mixed, in a platinum dish, with rather concentrated, slightly fuming hydrofluoric acid, the acid being added gradually, and the mixture stirred with a thick platinum wire. The mixture, which has the consistence of a thin paste, is digested some time on a water-bath at a gentle heat, and pure hydrated sulphuric acid, diluted with an equal quantity of water, is then added drop by drop, in more than sufficient quantity to convert all the bases present into sulphates. The mixture is now evaporated on the water-bath to dryness, during which operation fluoride of silicon gas and hydrofluoric acid gas are continually volatilizing; then it is finally exposed to a stronger heat, over the lamp, with proper caution, until the excess of sulphuric acid is completely expelled. The mass, when cold, is thoroughly moistened with concentrated hydrochloric acid, and allowed to stand at rest for one hour; water is then added, and a gentle heat applied. If the decomposition has fully succeeded, the whole must dissolve to a clear fluid. If an undissolved residue is left, the mixture is heated for some time on the water bath, then allowed to deposit, the clear supernatant fluid decanted off as far as practicable, the residue dried, and then treated again with hydrofluoric acid and sulphuric acid, and, lastly, with hydrochloric acid, which will now effect complete solution, provided the analysed substance was very finely pulverized, and free from baryta, strontia (and lead). The solution is added to the first. The bases in the solution (which contains them as sulphates, and contains also free hydrochloric acid), are determined by the methods which will be found in Section V.

This method, which is certainly one of the best to effect the decomposition of silicates, has *Berzelius* for its author. It has been but little used hitherto, because we did not know how to prepare hydrofluoric acid, except with the aid of a distilling apparatus of platinum, or, at least with a platinum head; nor to keep it, except in platinum vessels. This difficulty, however, would appear to be overcome now, since *Städeler* ("Annal. d. Chem. und Pharm.," 87, 137) has made the discovery that gutta percha and vulcanized india-rubber resist the action of hydrofluoric acid. *Städeler* prepares the acid in a leaden retort having the shape of a digesting glass with the neck cut off. The retort has about 5 inches inner diameter; the width of the very short neck is 1¾ inches. A close-fitting wide leaden pipe, 4 inches long, is put into the mouth of the neck, which is turned perfectly even and smooth inside; the upper end is a little contracted, so that it may be closed with a common cork, which bears a double-limbed thin leaden pipe. The length of the longer limb is 6 inches; this limb is connected with a tube of stout vulcanized india-rubber, which opens into the gutta-percha vessel intended to receive the hydrofluoric acid, but barely dips into the water in the receiver, by which precaution the receding of the acid is guarded against. Care must be taken to keep the receiver properly cooled. The gutta-percha vessels in which the acid is kept have the form of common bottles, and are closed with gutta-percha stoppers.*

The execution of the method requires the greatest possible care, both the liquid and the gaseous hydrofluoric acid being most dangerous substances. The treatment of the silicate with the acid and the evaporation must be conducted in the open air, otherwise the windows and all glass vessels and glass apparatus will be greatly injured. As the silicic acid is in this method simply inferred from the loss, a combination of the two methods, α and β, *aa* is often resorted to.

bb. By Hydrofluoric Acid Gas.

Instead of the hydrofluoric acid dissolved in water, the gaseous acid also may be used to effect the decomposition of silicates. *Brunner* ("Pogg. Annal.," 44, 134) is the author of this method, which is very often employed. The process is as follows:—Put from 1 to 2 grammes of the silicate, very finely pulverized, in the thinnest possible layer, into a shallow platinum dish, and moisten the powder with water or with dilute sulphuric acid; place the dish, supported on a leaden tripod or leaden ring, in the centre of a leaden box, which may have a diameter of 6 inches and a height of 6 inches, and on the bottom of which you have just before spread a layer of about half an inch of powdered fluor-spar, made into a thick paste with concentrated sulphuric acid; in this latter operation, be cautious to avoid the escaping vapors; the mixing of the powdered fluor-spar with the sulphuric acid is effected with a long glass rod, or, better still, with a long leaden rod. As soon as you have placed the small dish into the box, with the aid of a pair of pincers, put on the tightly fitting leaden cover, lute the joinings with gypsum paste, and put the box in a warm place for from 6 to 8 days. If you wish to accelerate the process, you must not lute the joinings quite air-tight, and must heat the apparatus in the *open air* by means of a small spirit-lamp; in this manner you may succeed in a few hours to effect the decomposition of from 1 to 2 grammes of the powdered silicate, provided it is spread in a very thin layer, or stirred from time to time, which latter operation, however, requires caution.

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* These bottles may be procured at the Gutta-percha Works, City Road.

If the decomposition has succeeded well, the residue in the platinum dish consists of metallic silico-fluorides and (if you have used sulphuric acid to moisten the powder) sulphates. Put the shallow dish now into a larger platinum dish, add, drop by drop, pure sulphuric acid, in somewhat more than sufficient quantity to effect the conversion of the bases into sulphates; evaporate in the air-bath, expel finally the excess of hydrated sulphuric acid over the lamp, and treat the residue with hydrochloric acid and water in the manner directed in β, *aa*. The decomposition can only be considered complete if the residue is entirely dissolved.

γ. *Decomposition and Solution of Silicates by fusion with Hydrate of Baryta or Carbonate of Baryta.*

The fusion of silicates with carbonate of baryta requires a very high degree of heat, attainable only by means of a *Sefström* furnace, or a *Griffin's* gas-furnace or a blast gas-lamp, or a *Deville* turpentine lamp, &c.; as the highest temperature attainable by means of a wind furnace fails to fuse carbonate of baryta, and it is only in a state of fusion that this reagent effects complete decomposition of silicates. But then, on the other hand, the action of carbonate of baryta in a state of fusion is so energetic, that even the most refractory siliceous minerals are readily and completely decomposed by it. The proportion is from 4 to 6 parts of carbonate of baryta to 1 part of the mineral. The fusion is effected in a platinum crucible, which, if a *Sefström* furnace is used, is inserted in another crucible of refractory fire-clay, filled with magnesia. The crucible is left in the fire a quarter of an hour at least.

With more readily decomposable minerals, the object in view may be attained more easily with hydrate of baryta freed from its water of crystallization. From 4 to 5 parts of the hydrate are intimately mixed with 1 part of the mineral; it is advisable to cover the mixture with a layer of carbonate of baryta. The fusion may be effected over a common gas- or *Berzelius* spirit-lamp; silver crucibles are preferable to platinum, as the latter are slightly affected by the operation. The mixture fuses completely, or, at least, its particles agglutinate into a semi-fused mass.

When the operation is terminated—no matter whether carbonate or hydrate of baryta has been employed—the crucible is allowed to cool, carefully cleaned outside, and put with its contents into a beaker, where it is then covered with from 10 to 15 parts of water; hydrochloric or nitric acid is added, and the rest of the operation conducted as in *b*, *a*. Care must be taken, however, not to add too much hydrochloric acid at once, as the chloride of barium formed is difficultly soluble in that acid, and would consequently tend to impede further solution, by forming a kind of insoluble protecting crust round the still undissolved portion. In the solution filtered from the silicic acid, the bases are determined by the methods which will be found in Section V. The purity of the silicic acid obtained must be tested as directed in *a*, before the operation can be looked upon as successful. These methods, which were formerly often employed to determine the alkalies in silicates, have been in a measure superseded by β, *bb* (decomposition by hydrofluoric acid gas).

Deville ("Ann. de Chim. et de Phys.," 3 Sér., 38, 5) has lately called attention to the fact that the quantity of carbonate of baryta usually employed to effect the decomposition of silicates (from 4 to 6 parts) is much larger than required. He states that 1 part of *orthoclase* fuses, at a moderate red heat, with as little as 0·8 parts of carbonate of baryta to a vitreous transparent mass, decomposable by acids. He adds that, if the carbonate is used in larger proportions, an appreciable amount of potassa volatilizes, expelled by the agency of caustic baryta formed in the process. *Smith* ("Journ. f. prakt. Chem.," 60, 246)* recommends to fuse 1 part of the silicate with from 3 to 4 parts of carbonate of baryta and 2 parts of chloride of barium.

δ. Decomposition and Solution of Silicates by fusion with Lime and Lime Salts.

Deville ("Ann. de Chim. et de Phys.," 3 Sér., 38, 5) recommends also to fuse 1 part of the powdered silicate with from 0·3 to 0·8 parts of carbonate of lime. I have tried this process, but have not found it answer in the case of many silicates. *L. Smith* ("Journ. f. prakt. Chem.," 60, 246)† recommends to fuse 1 part of the powdered silicate with from 5 to 6 parts of carbonate of lime, and from 0·5 to 0·7 of chloride of ammonium, for 30 or 40 forty minutes, at a bright red heat; boil the fused mass for 2 or 3 hours with water, taking care to replace the loss from evaporation; fuse the residue once more with half its weight of chloride of ammonium, and boil the fused mass again with water. He states that, if no boracic acid is present, the whole of the alkalies will be found in the aqueous solution. *J. Tipp* ("Vierteljahrsschrift f. prakt. Pharm.," IV., 68) confirms this statement.

SECOND GROUP.

HYDROCHLORIC ACID—HYDROBROMIC ACID—HYDRIODIC ACID—HYDROCYANIC ACID—HYDROSULPHURIC ACID.

§ 141.

1. HYDROCHLORIC ACID.

I. *Determination.*

Hydrochloric acid may be determined very accurately in the gravimetrical, as well as in the volumetrical way.‡

a. Gravimetrical Method.

Determination of Silver as Chloride.

Solution of nitrate of silver, mixed with some nitric acid, is added in excess to the solution under examination, the precipitated chloride is made to subside by application of heat and shaking, washed by decantation, dried and ignited. The details of the process have been given in § 115, 1, *a*, *a*. Care must be taken not to heat the solution mixed with nitric acid, before the solution of nitrate of silver has been added in excess. As soon as the latter is present in excess, the chloride of silver separates immediately and completely upon shaking the vessel, and the supernatant fluid becomes perfectly clear after standing a short time in a warm place. The determination of hydrochloric acid by means of silver is therefore more readily effected than that of silver by means of hydrochloric acid. In the case of smaller quantities of chloride of silver, the precipitate is often collected on a filter; see § 115, 1, *a*, *β*. Or the two methods may be combined in this way—that the chief portion of the precipitate is washed by decantation, dried in the porcelain crucible, and ignited, the decanted fluid being afterwards passed through a filter, to make quite sure that not a particle of chloride of silver has been lost. The filter is, after drying, incinerated in a platinum wire over the inverted cover of the porcelain crucible, the ashes are treated with a few drops of nitric acid, some hydrochloric acid is added, the mixture evaporated to dryness, the residue gently ignited, and the lid replaced in the proper position on the crucible in which the chloride has been heated to incipient fusion; a gentle heat is then once more applied, after which the crucible is allowed to cool under the desiccator, and then weighed.

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* *Silliman's* "American Journal," 1853, vol. xvi. page 53. † Ibid.

‡ For the acidimetric estimation of free hydrochloric acid, see § 215.

b. Volumetrical Method of estimating Hydrochloric Acid.

a. By Solution of Nitrate of Silver.

In § 115, 5, we have seen how the silver in a fluid may be estimated by adding a solution of chloride of sodium of known strength until no further precipitation ensues; in the same way we may determine also, by means of a solution of silver of known strength, the amount of hydrochloric acid in a fluid, or of chlorine in combination with a metal.

Pelouze has used this method for the determination of several equivalent numbers. *Levol* has proposed a modification which serves to indicate more readily and accurately the exact point of complete precipitation. This modification consists in the addition of 0·1 volume of a saturated solution of phosphate of soda to the *neutral* fluid. When the whole of the chlorine has been precipitated by the silver, the addition of another drop of the solution of silver produces a yellow precipitate which does not disappear upon shaking the vessel ("Journ. f. prakt. Chem.," 60, 384). *Fr. Mohr* has since replaced, with the most complete success, the phosphate of soda by chromate of potassa.

This convenient and accurate method requires two solutions of known strength, viz., one of chloride of sodium, and another of nitrate of silver, free from excess of acid.

The best way is to use the decimal standard solutions mentioned in § 115, *b*, *5*, *d*, which contain in 1 litre of fluid, respectively, 5·846 grm. of chloride of sodium, and 10·797 grm. of silver. As the silver solution must be free from acid, it is advisable to prepare it by dissolving 10·797 grm. of pure silver in dilute nitric acid, in a flask placed in a slanting position; evaporating the solution, in a large porcelain dish, cautiously, to dryness (until no more acid fumes escape), dissolving the residue in water, transferring the solution to the litre-flask, diluting to the mark, and shaking.

Before the standard solutions of chloride of sodium and nitrate of silver can be employed, their strength must be tested. This is done by mixing 20 c.c. of the one with 20 c.c. of the other, shaking the mixture, applying heat, letting the precipitate subside, decanting, and adding to one portion of the clear fluid a drop of solution of nitrate of silver, to the other a drop of solution of chloride of sodium. If the solutions are of the exact strength indicated, and the measuring vessels quite accurate, both portions of the fluid must remain clear.

It is now, in the first place, necessary to study the exact point of the completion of the chromate of potassa reaction. To this end, about 10 cub. cent. of fluid are allowed to flow out from the burette containing the standard solution of chloride of sodium; the height of the fluid is read off with the greatest accuracy, 4 or 5 drops of a cold saturated solution of pure neutral chromate of potassa are added, and then to the bright yellow fluid, from another burette, drop by drop, standard solution of nitrate of silver. As each drop falls into the fluid, it produces a red spot, which disappears again on stirring, owing to the instant decomposition of the newly-formed chromate of silver with the chloride of sodium. At last, however, the red coloration remains, which is a sign that the whole of the chlorine present has combined with the silver, and that a little chromate of silver has been permanently formed. On reading off now, it is constantly found that there has been consumed in the process almost exactly 0·1 cub. centimet. more of the silver solution than of the chloride of sodium solution. This trifling excess arises from the fact that it requires 0·1 of solution of nitrate of silver to produce a sufficient quantity of chromate of silver to impart a distinct red coloration to the fluid. If the red coloration is too strongly marked, solution of chloride of sodium may be added, drop by drop, until it has disappeared again; addition of 0·1 cub. cent. of the silver solution will then reproduce the red tint. As the two standard solutions are of equal value, the supplementary quantity of chloride of sodium solution added need simply be subtracted from the silver solution.

With a correct appreciation of the transition point from yellow to red, it is an easy task to estimate with great accuracy hydrochloric acid, or chlorine in metallic chlorides soluble in water. It must be borne in mind, however, that the fluid must be neutral or very slightly alkaline, but on no account acid, as free acids dissolve chromate of silver. The solution of the weighed sample under examination must, therefore, if required, be made quite neutral or very slightly alkaline, by addition of nitric acid or of carbonate of soda. 4 or 5 drops of solution of neutral chromate of potassa are then added to the fluid, and afterwards solution of nitrate of silver, drop by drop, from the burette, until the exact point is reached at which the red color becomes permanent. 0·1 cub. cent. is deducted from the number of cubic centimetres of silver solution used in the process; the remainder shows the quantity of the hydrochloric acid, or of the chlorine in the examined chloride; since 1000 cub. cent. of the solution of nitrate of silver corresponds respectively to 3·646 $H\,Cl$,—3·546 chlorine,—5·846 $Na\,Cl$, &c., *i.e.* to the decimal equivalent numbers of the substances sought.

Should a loss have occurred in the evaporation of the silver solution, the correct strength must be determined again by making it act repeatedly upon 20 cub. cent. of the standard solution of chloride of sodium. The proportion found forms the basis of the calculations, in the determinations of chlorine by the solution. In such cases, however, the subtraction of 0·1 c.c. of silver solution is omitted in the first, as well as in all the subsequent experiments. *Fr. Mohr* obtained very satisfactory results by this method, and I can say the same of the experiments made with it in my own laboratory.

β. *By Solution of Nitrate of Silver and Iodide of Starch* (*Pisani's* method—"Annal. d. Mines," X. 83.—*Liebig* and *Kopp's* "Jahresbericht" f. 1856, 751).

Add to the solution of the chloride, acidified with nitric acid, a slight excess of solution of nitrate of silver of known strength, warm, and filter. Determine the excess of silver in the filtrate by means of solution of iodide of starch (see § 163, Separation of Silver from Lead), and deduct this from the amount of silver solution used. The difference shows the quantity of silver which has combined with the chlorine; calculate from this the amount of the latter. Results satisfactory.

γ. *With Solution of Nitrate of Oxide of Mercury* (*Liebig's* method—"Annal. d. Chem. u. Pharm.," 85, 297); recommended more particularly for the determination of chlorine in the chlorides contained in the urine.

aa. Principle of the method. Nitrate of oxide of mercury immediately produces in a solution of urea a thick white precipitate; solution of chloride of mercury produces no such precipitate. When a solution of nitrate of oxide of mercury is mixed with the chloride of an alkali, there is formed *chloride of mercury* and nitrate of the alkali. If, therefore, a solution of urea is mixed with chloride of sodium, and a dilute solution of nitrate of oxide of mercury is added, drop by drop, the fluid will show in the points of contact a white turbidity, which, however, will immediately disappear upon shaking, so long as the nitrate of oxide of mercury continues to decompose and transpose with the chloride of sodium in the manner just stated; but the moment this double decomposition is complete, an additional drop of the solution of the salt of mercury will produce a permanent white turbidity. Accordingly, if we know the measure and strength of the solution of the salt of mercury required to attain this point, we know also the amount of chlorine in the solution; since 1 equivalent of mercury in the mercurial solution corresponds to 1 equivalent of chlorine.

bb. Preparation of the solution of nitrate of oxide of mercury. As this solution must be perfectly free from other metals, it is advisable to prepare it with oxide of mercury—precipitated from solution of crystallized chloride of mercury by solution of soda, and thoroughly washed—by dissolving 10·8 grm. of the dry oxide in nitric acid, evaporating the solution to the consistence of syrup, and diluting with water to the volume of 550 cubic centimetres. Or the solution may be made by dissolving repeatedly recrystallized nitrate of suboxide of mercury in water, with addition of nitric acid, heating to boiling, adding strong nitric acid until no more red fumes escape, evaporating to the consistence of syrup, and diluting with a proper quantity of water to give a solution of tolerably correct concentration.

cc. Determination of the strength of the solution. This is effected with the aid of a solution of chloride of sodium of known strength, which *Liebig* prepares by mixing 20 cubic centimetres of a *saturated** solution of pure rock salt or chemically pure chloride of sodium, with 298·4 cubic centimetres of water. Every cubic centimetre of this solution contains 20 milligrammes of chloride of sodium.

Of this solution of chloride of sodium measure 10 cubic centimetres into a small beaker, and add 3 c.c. of a solution of urea containing in 100 c.c. 4 grammes of urea.

Let the solution of mercury, of which you wish to ascertain the strength, drop into this mixture, from a burette, or from a pipette provided with a caoutchouc connector and a clamp, until a perceptible precipitate forms, which on shaking fails to redissolve.†

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* Saturated at the common temperature.

† A mere opalescence of the fluid is disregarded, as this proceeds simply from a trace of foreign metals, which is readily seen from the circumstance that a further addition of the mercurial solution does not increase the turbidity.

dd. When you have in this way ascertained how many c.c. of the mercurial solution correspond to the 10 c.c. of the solution of common salt = 0·2 grm. of chloride of sodium, you may use the mercurial solution without further preparation, if you do not mind the trouble of a little calculation. But if you wish to avoid this, you must previously dilute the mercurial solution in a manner that every cubic centimetre corresponds to an integral number of milligrammes of chloride of sodium or chlorine. *Liebig* dilutes it to the extent that 1 cubic centimetre corresponds to 0·010 grm. of chloride of sodium.

ee. If the test fluid is intended to examine solutions containing a large amount of foreign salts, or an excess of urea, the 10 c.c. of the chloride of sodium solution must be mixed with 5 c.c. of a cold saturated solution of sulphate of soda,* in addition to the 3 c.c. of solution of urea, before the mercurial solution is added. The results are accurate.

If you have a decimal standard solution of chloride of sodium, containing 5·846 grm. in the litre, you may, of course, also determine the strength of the mercurial solution by means of this.

Fr. Mohr uses ferricyanide of potassium instead of urea. This reagent requires, however, still greater purity of the mercurial solution than is the case where urea is used ; otherwise permanent precipitates of ferricyanides are formed from the beginning, which of course obscure the final reaction.

Of these volumetrical methods of estimating chlorine, the first deserves the preference in all ordinary cases. It cannot be employed, however, in analyses of urine, as compounds of oxide of silver with coloring matters, &c., precipitate along with the chloride of silver (*C. Neubauer*). *Pisani's* method (*b*, *β*) is especially suited for the estimation of very minute quantities of chlorine.

II. *Separation of Chlorine from the Metals.*

a. In Soluble Chlorides.

The same method as in I., *a.* The metals in the filtrate are separated from the excess of the salt of silver by the methods which will be found in Section V.

Bichloride of tin, *chloride of mercury*, the *chlorides of antimony*, and the *green protochloride of chromium*, form exceptions from the rule, and are determined respectively by the following methods :—

a. From solution of *bichloride of tin*, nitrate of silver would precipitate, besides chloride of silver, a mixture of binoxide of tin and oxide of silver. To precipitate the tin, therefore, the solution is mixed with a concentrated solution of sulphate of soda, or nitrate of ammonia, allowed to deposit, the fluid decanted, and filtered (compare § 126, *b*, 1, *b*), and the chlorine in the filtrate precipitated with solution of silver. *Löwenthal*, the inventor of this method, has proved its accuracy ("Journ. f. prakt Chem.," 56, 371).

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* The reason of this addition is, that the nitrate of oxide of mercury and urea is more readily soluble in pure water than in saline solutions ; to attain accurate results, therefore, it is necessary that the solvent power of the fluids should be as nearly as possible the same in the preliminary determination of the strength of the mercurial solution as in the subsequent analytical process.

β. When a solution of *chloride of mercury* is precipitated with solution of nitrate of silver, the chloride of silver thrown down contains an admixture of mercury. The mercury is, therefore, first precipitated by sulphuretted hydrogen, which must be added in sufficient excess, and the chlorine in the filtrate determined as directed in § 165.

γ. The chlorides of antimony are also decomposed in the manner described in *β*. The separation of basic salt upon the addition of water may be avoided by addition of tartaric acid.

δ. Solution of silver fails to precipitate the whole of the chlorine from solution of the *green protochloride of chromium* (*Péligot*). The chromium is, therefore, first precipitated with ammonia, the fluid filtered, and the chlorine in the filtrate precipitated as directed in I., *a.*

b. In Insoluble Chlorides.

a. Chlorides soluble in Nitric Acid.

Dissolve the chloride in nitric acid, without applying heat, and proceed as directed in I., *a.*

β. Chlorides insoluble in nitric acid (chloride of lead, chloride of silver, subchloride of mercury).

- *aa.* Chloride of lead is decomposed by digestion with alkaline bicarbonates and water. The process is exactly the same as for the decomposition of sulphate of lead (§ 132, 11, *b*, *β*).
- *bb.* Chloride of silver is ignited in a porcelain crucible, with 3 parts of carbonate of soda and potassa, until the mass commences to agglutinate. Upon treating the mass with water, the metallic silver is left undissolved; the solution contains the alkaline chloride, which is then treated as directed in II., *a.*

Chloride of silver may also be readily decomposed by digestion with pure zinc, and dilute sulphuric acid. The separated metallic silver may be weighed in that state; it must afterwards be ascertained, however, whether it dissolves in nitric acid to a clear fluid. The chlorine is determined in the solution of chloride of zinc obtained, as in II., *a.*

- *cc.* Subchloride of mercury is decomposed by digestion with solution of soda or potassa. The hydrochloric acid in the filtrate is determined as in II., *a.* The suboxide of mercury is dissolved in nitro-hydrochloric acid, and the mercury determined as directed in § 118.

c. The soluble chlorides of the metals of the fourth, fifth, and sixth groups may all be decomposed also by sulphuretted hydrogen, or, as the case may be, sulphide of ammonium. The hydrochloric acid in the filtrate is determined as directed in § 169.

d. In many metallic chlorides, for instance, in those of the first and second groups, the chlorine may be determined also by evaporating with sulphuric acid, converting the base thus into a sulphate, which is then ignited and weighed; the chlorine being calculated from the loss. This method is not applicable in the case of chloride of silver and chloride of lead, which are only imperfectly and with difficulty decomposed by sulphuric acid; nor in the case of chloride of mercury and bichloride of tin, which sulphuric acid fails altogether to decompose, or decomposes only to a barely perceptible extent.

Supplement.

Determination of Chlorine in the Free State.

§ 142.

Chlorine in the free state may be determined both in the volumetrical and in the gravimetrical way. The volumetrical methods, however, deserve the preference in most cases. They are very numerous. The following are the best.*

1. *Volumetrical Methods.*

a. With Iodide of Potassium and Iodine (*Bunsen's* method).

Bring the chlorine, in the gaseous form or in aqueous solution, into contact with an excess of solution of iodide of potassium in water (compare § 130, *d*, *β*). Each equivalent of chlorine liberates 1 equivalent of iodine. By determining the liberated iodine, by the method given in § 146, you will accordingly learn with the greatest accuracy the quantity of the chlorine.

b. With Arsenite of Soda and Iodine (*Fr. Mohr's* method, slightly modified).

The process requires,—

aa. A solution of iodine in iodide of potassium of most accurately known strength. The same solution is usually employed, which serves for the estimation of iodine, &c., by *Bunsen's* method (see § 146). It contains, in the cubic centimetre, about 0·005 grm.† of iodine, which we will here assume to be the fixed standard of it. This, calculated for chlorine, corresponds to 0·00139 grm. of chlorine.

bb. A solution of arsenite of soda. This is prepared by boiling 5 grammes of pure arsenious acid with 10 grammes of bicarbonate of soda in water, until complete solution is effected. The solution is then diluted with water to the volume of a litre. This solution has at first a fixed strength; but there is no reliance to be placed upon its retaining this strength for any length of time, as it would appear that arsenite of soda will, under certain circumstances not yet quite settled, attract oxygen from the atmosphere, with greater or less rapidity, and suffer conversion, to a greater or less extent, into arsenate of soda.‡

The relative proportion between the solution of arsenite of soda and the iodine solution must, therefore, be determined before every fresh series of experiments, the known strength of the iodine solution being always taken for the basis. To this end, 10 cubic centimetres of the arsenical solution are measured off, slightly diluted, 10 c.c. of a cold saturated solution of bicarbonate of soda added, then a little starch paste, and the iodine solution drop by drop, until a permanent blue coloration is produced. Suppose 26 c.c. of iodine solution have been used to 10 c.c. of the arsenite of soda solution, to produce this result.

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* Compare article "Chlorimetry" in the Special Part, § 224.

† *Mohr* recommends the use of a solution of iodine containing only $\frac{1}{100}$ equivalent = 1·269 grm. in the litre. This does not appear to me very practical, as it necessitates a repeated filling of the burette in almost every experiment. It would appear also, from *Mohr's* own showing, that he himself usually employs a more concentrated solution.

‡ *Fresenius*, "Annal. d. Chem. u. Pharm.," 93, 384. *Fr. Mohr*, ibid., 94, 222. *W. Mayer*, ibid. 101, 266.

Now, if it is wished to determine by this method the quantity of chlorine in a solution, a definite amount, say 30 c.c., of the arsenite of soda solution is measured off, about an equal amount of a cold saturated solution of bicarbonate of soda added, then a certain measured or weighed quantity, say 20 grammes, of the chlorine water. (The solution of the arsenite of soda must of course be in excess; whether this is the case, is ascertained by letting a drop of fluid fall upon a slip of iodide of potassium and starch paper,* which must not be tinged blue by it. Should a blue tint be imparted to the paper, an additional measured quantity of the arsenite of soda solution must be added.) The fluid is now mixed with some starch paste, and iodine solution added, until a permanent blue coloration is produced. Suppose there has been consumed in this operation 15 c.c. of iodine solution, it will at once be seen that the difference between the quantity of iodine solution which would have been required for the arsenite of soda solution used (in the case before us, 78 c.c., since 10 : 26 :: 30 : 78), and the quantity actually used—after the addition of the chlorine water—(in the present case, accordingly, $78 - 15 = 63$ cubic centimetres), gives the measure for the quantity of chlorine contained in the chlorine water, 1 equivalent of iodine = 126·88, corresponding of course to 1 equivalent of chlorine = 35·46. Now, in the case before us, the quantity of iodine solution saved, viz. 68 cubic centimetres, contains $63 \times 0{\cdot}005 = 0{\cdot}315$ grm. of iodine, which, as 0·005 grm. of iodine corresponds to 0·00139 grm. of chlorine, corresponds to $63 \times 0{\cdot}00139 = 0{\cdot}08757$ grm. of chlorine. As this quantity was contained in 20 grammes of the chlorine water, 100 grammes of the latter contain 0·43785 grms. of chlorine.

In cases where the chlorine to be estimated is evolved as gas, as in the analysis of chromic acid (§ 130, *d*, *β*), or of peroxides, *Fr. Mohr* uses the absorption apparatus shown in Fig. 71.

The large flask should hold about 1 litre; the wide open tube, fixed by the narrow lower end in the perforated cork of the large flask, is filled with fragments of glass.

An excess of arsenite of soda solution is poured into the flask, and a sufficient quantity of solution of carbonate of soda added, through the tube filled with fragments of glass. The small flask serves as evolution flask; in the analysis of chromates, for instance, the chromate is boiled in it with strong hydrochloric acid. When the gas-conducting tube has become hot in its entire length, and the contents of the large flask begin to effervesce strongly (a sign that hydrochloric gas passes over), and the vapors are absorbed with crackling noise, the little caoutchouc connector is closed with the clamp, the lamp removed immediately after, and the tube disconnected which leads from the small flask to the caoutchouc connector. The fragments of glass are then thoroughly washed, the rinsings running, of course, into the flask, which is allowed to stand with occasional moderate shaking, until it is quite cold. The tube dipping in the fluid is now also taken away and rinsed, the rinsings being added to the contents of the large flask. Some starch paste is now added, and then iodine solution until a permanent blue coloration is produced. The final reaction can be looked upon as conclusive only if the coloration does not disappear again upon addition of solution of carbonate, or, better still, bicarbonate of soda. On disconnecting the apparatus, neither the large nor the small flask must emit the odor of chlorine; otherwise the experiment is a failure. To afford some indication of the quantities to be used, I may remark that, in the analysis of bichromate of potassa, for instance, 0·2—0·5 grm. of that salt may be taken, to 40—100 c.c. of arsenite of soda solution in the receiver.

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* This is prepared by mixing 3 grms. of pure potato starch in 250 cubic centimetres of cold water, boiling with stirring, adding a solution of 1 grm. of iodide of potassium and 1 grm. of crystallized carbonate of soda, diluting the mixture to about 500 cubic centimetres, soaking fine white unsized paper in the fluid, and drying.

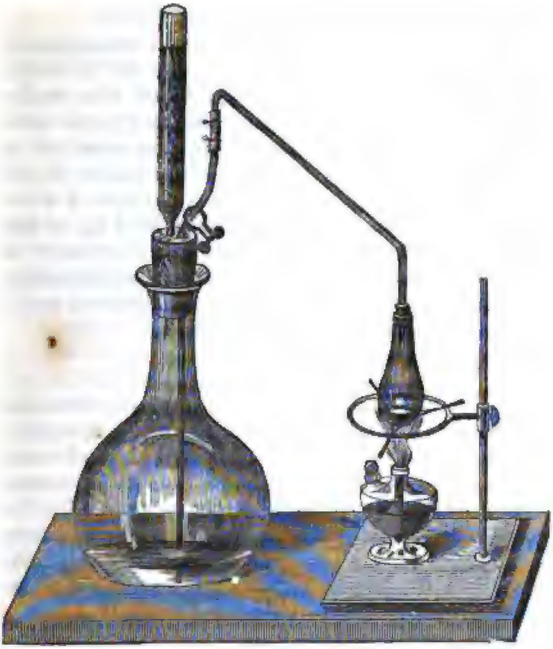

Fig. 71.

Note to a and b.

Upon an attentive consideration and comparison of the two preceding methods, *a* and *b*, it will be seen that in the former the quantity of iodine is to be determined which has been liberated by chlorine; whilst in the latter, on the contrary, we have to deal, not with the arsenious acid which has been oxidized, but with the excess of the acid which has not been oxidized. Now, although this is of no great consequence in cases where the amount of chlorine is comparatively large, it is of very considerable importance in cases where the amount of chlorine is only small, more particularly where it unexpectedly turns out to be so, and where, accordingly, a pretty large quantity of arsenate of soda solution has been employed in the analytical process. For, in such cases, it may happen that the small difference which lies within the limits of the errors of observation, and which, under the circumstances, on account of the indefinite and uncertain quantity of carbonate of soda added, is likely to rise to as high as 0·5 c.c., amounting to $\frac{1}{10}$, $\frac{1}{5}$, and even more of the difference between the quantities of the iodine solution respectively consumed in the experiments, before and after addition of the chlorine water; which may lead to very serious errors in the results, to the extent, indeed, of 10 or 20 per cent., and even more.

For this reason *Bunsen's* method (*a*) alone deserves to be recommended for the estimation of *smaller* quantities of chlorine.

c. With Solution of Protoxide of Iron and Permanganate of Potassa. The chlorine solution is mixed with an excess of solution of protochloride of iron, or sulphate of protoxide of iron and ammonia of known strength, in a stoppered flask; the mixture is allowed to stand for some time, and the iron, still left in the state of protochloride or protoxide, determined by solution of permanganate of potassa (§ 112). It must be borne in mind, in the calculation, that 2 eq. of protochloride of iron are converted into sesquichloride by 1 eq. of chlorine. This method is suited, indeed, for the estimation of chlorine in aqueous solution; but it is much less adapted to effect the determination of chlorine when evolved in gaseous form, as the gas is absorbed with comparative slowness by the protochloride of iron solution.

2. *Gravimetrical Method.*

The fluid under examination, which must be free from sulphuric acid, say, for instance, 30 grammes of chlorine water is mixed in a stoppered bottle, with an excess, say 0·5 grm., of hyposulphite of soda, the stopper inserted, and the bottle kept for a short time in a warm place; after which the odor of chlorine is found to have gone off. The mixture is then heated to boiling with some hydrochloric acid in excess, to destroy the excess of hyposulphite of soda, filtered, and the sulphuric acid in the filtrate determined by baryta (§ 132). 1 equivalent of sulphuric acid corresponds to 2 equivalents of chlorine (*Wicke*, "Annal. d. Chem. u. Pharm.," 99, 99).

In fluids containing, besides free chlorine, also hydrochloric acid, or a metallic chloride, the chlorine existing in a state of combination may be determined, in presence of the free chlorine, in the following way:—

a. A weighed portion of the fluid is mixed with ammonia in excess;* nitrogen escapes, and the solution contains the whole of the free chlorine as chloride of ammonium ($3\,Cl + 4\,N\,H_3 = N + 3\,[N\,H_4\,Cl]$). By precipitating now with solution of silver, we learn the total amount of the chlorine. The quantity of the free chlorine is then determined in another weighed portion, by means of iodide of potassium, or by some other method; the difference gives the amount of chlorine which the analysed fluid contained in a state of combination.

b. A weighed portion of the fluid is mixed with solution of sulphurous acid in excess, the mixture acidified with nitric acid, and the whole of the chlorine precipitated as chloride of silver. The further operation is conducted as in *a.*

Having thus seen in how simple a manner the quantity of free chlorine may be determined by *Bunsen's* method, and for larger amounts also by *Mohr's* method, it will be readily understood that all oxides and peroxides which evolve chlorine when heated with hydrochloric acid, may be analysed by heating them with concentrated hydrochloric acid, and determining the amount of chlorine evolved. For the *modus operandi* compare § 130, *d*, *β*, and § 142, *b*.

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* If chlorine water is mixed at once with solution of nitrate of silver, $\frac{5}{6}$ths only of the chlorine are obtained as chloride of silver: $6\,Cl + 6\,Ag\,O = 5\,Ag\,Cl + Ag\,O, Cl\,O_5$ (*H. Rose; Weltzien*, "Annal. d. Chem. u. Pharm.," 91, 45).

§ 143.

2. HYDROBROMIC ACID.

I. *Determination.*

a. Free hydrobromic acid is precipitated from its solution with nitrate of silver, and the further process conducted as in the case of chlorine (§ 141). For the properties of bromide of silver, see § 94, 2. The results are perfectly accurate.

b. Heine's colorimetrical method.[*] The bromine is liberated by means of chlorine, and received in ether; the solution is compared, with respect to color, with an ethereal solution of bromine of known strength, and the quantity of bromine contained in it thus ascertained. *Fehling* ("Journ. f. prakt. Chem.," 45, 269) obtained satisfactory results by this method. It will at once be seen that the amount of bromine contained in the fluid to be analysed must be known in some measure, before this method can be resorted to. As the mother liquor examined by *Fehling* could contain at the most 0·02 grm. of bromine, he prepared ten different test fluids, by adding to ten several portions of 60 grammes each of a saturated solution of common salt increasing quantities of bromide of potassium (containing respectively from 0·002 grm. to 0·020 grm. of bromine). He added an equal volume of ether to the test fluids, and then chlorine water, until there was no further change observed in the color of the ether. It being of the highest importance to hit this exact point, *Fehling* prepared three samples of each test fluid, and then chose the darkest of them for the comparison. 60 grammes are now taken[†] of the mother liquor to be examined, the same volume of ether added as was added to the test fluids, and then chlorine water. Every experiment is repeated several times. Direct solar light must be avoided, and the operation conducted with proper expedition.

c. Figuier's colorimetrical method ("Annal. de Chim. et de Phys.," 33, 303, and "Journ. f. prakt. Chem.," 54, 293), proposed as a useful method to effect the determination of bromine in mother liquors, &c.

This method is based upon the circumstance that 1 equivalent of chlorine (added in the form of chlorine water), liberates from a solution of a metallic bromide 1 equivalent of bromine, and that bromine imparts a yellow color to an aqueous solution, and escapes readily upon boiling, the yellow tint of the solution disappearing again with the escape of the bromine.

To carry this method into effect, the strength of the chlorine water is determined at the moment of its application, by making it act upon a solution of bromide of sodium of known strength, acidified with a few drops of hydrochloric acid (or by one of the methods given in § 142), and then applying it to the mother liquor. The latter is heated in a flask nearly to ebullition; chlorine water is then added from a burette covered with black paper, and the mixture heated for about 3 minutes, whereupon the yellow tint imparted to the fluid by the addition of the chlorine water will disappear again; the mixture is now allowed to cool for 2 minutes, after which some more chlorine water is dropped into it, heat again applied, and the same process repeated until further addition of chlorine water fails to impart a yellow color to the fluid. Should the experiment last several hours, the strength of the chlorine water must be determined once more at the end of the process, and the calculation of the results based upon the mean of the two experiments. Alkaline fluids must be slightly acidified with hydrochloric acid. Protoxide of iron, protoxide of manganese, iodine, and organic matters must not be present. Mother liquors colored yellow by organic matter should be evaporated to dryness, the residue gently ignited, then treated with water, and the fluid filtered. In evaporating the solutions to dryness, carbonate of soda must be added, since chloride and bromide of magnesium evolve hydrochloric and hydrobromic acids in the process.

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[*] "Journ. f. prakt. Chem.," 36, 184, proposed as a useful method to effect the determination of bromine in mother liquors.

[†] The best way is to take them by measure.

II. *Separation of Bromine from the Metals.*

The metallic bromides are analysed exactly like the corresponding chlorides (§ 141, II., *a* to *d*), the whole of these methods being applicable to bromides as well as chlorides. In the decomposition of bromides by sulphuric acid (§ 141, II., *d*), porcelain crucibles must be used instead of platinum ones, as the liberated bromine would injuriously affect the latter.

Supplement.

Determination of Free Bromine.

§ 144.

Free bromine in aqueous solution, or evolved in the gaseous form, is determined in the same way as free chlorine (see § 142).

Another method has been proposed by *Williams* ("Chem. Gaz.," 1854, 432). It is based upon the fact that free bromine suffers decolorization by the action of oil of turpentine, the bromine replacing the hydrogen in the latter—34 parts of oil of turpentine (1 equivalent) decolorize 79·97 parts (1 equivalent) of bromine. A solution of perfectly pure oil of turpentine in absolute alcohol is used as test fluid, 20 grammes of the oil being dissolved to 200 c.c. of fluid. The fluid containing the free bromine should be in a stoppered bottle. The test fluid is added drop by drop, the bottle being shaken after every addition, and the operation continued until the mixture is quite colorless. Every 34 c.c. correspond to 8 grms. of bromine. For small quantities of bromine a more dilute test fluid must be used. Results satisfactory.

The determination of free bromine in presence of hydrobromic acid or metallic bromides is also effected in the same manner as that of free chlorine in presence of hydrochloric acid or metallic chlorides (see § 142, 2). The addition of ammonia to the bromine requires caution. If bromine in solution is to be converted by ammonia into bromide of ammonium, the solution is poured into a capacious flask, a tolerably large quantity of water added, and then the ammonia through a funnel tube. The nitrogen gas escaping is transmitted, by means of a bent tube, through dilute ammonia; the two fluids are then mixed together, and the remaining part of the process is conducted as directed in § 142. By this means all loss of substance is effectively guarded against.

§ 145.

3. HYDRIODIC ACID.

I. *Determination.*

a. If you have hydriodic acid in solution, precipitate with nitrate of silver, and proceed exactly as with hydrochloric acid (§ 141). For the properties of iodide of silver, see § 94, 3. The results are perfectly accurate.

b. The following method, recommended first by *Lassaigne*, is resorted to almost exclusively to effect the separation of hydriodic acid from hydrochloric and hydrobromic acids, for which purpose it is extremely well adapted. Acidify the solution slightly with hydrochloric acid, and add a solution of protochloride of palladium, as long as a precipitate forms; let the mixture stand from 24 to 48 hours in a warm place, filter the russet-black precipitate off on a weighed filter, wash with warm water, and dry at a temperature from about 158° to 176° F., until the weight remains constant. The drying may be greatly facilitated by replacing the water (after the operation of washing) by some alcohol, and the latter fluid again by a little ether. For the properties of the precipitate, see § 94, 3. This method gives very accurate results, provided the drying be managed with proper care; but if the temperature is raised to near 212° F., the precipitate smells of iodine, and a trifling loss is incurred.

Instead of simply drying the protiodide of palladium, and weighing it in that form, you may ignite it in a crucible of porcelain or platinum,* and calculate the iodine from the residuary metallic palladium (*H. Rose*).

c. *Kersting's* volumetrical method ("Annal. der Chem. und Pharm.," 87, 25). This method is based upon the precipitation of iodine from iodide solution by protochloride of palladium. The process requires,—

α. *A solution of pure iodide of potassium* containing exactly 1 part of iodine in 1000 parts of fluid. This is prepared by dissolving 1·308 grm. of ignited iodide of potassium in water, and diluting the solution to 1 litre of fluid.

β. *An acid solution of protochloride of palladium* containing exactly 1 part of palladium in 2370 parts of fluid. This is prepared by dissolving 1 part of palladium in nitrohydrochloric acid, with application of heat, evaporating the solution to dryness at 212° F., adding 50 parts of concentrated hydrochloric acid and 2000 parts of water, and allowing to deposit. The exact strength of the clear solution is then ascertained by means of the solution of iodide of potassium, in the manner described below (*Analytical Process*).

γ. *The solution of the iodide to be analysed.* Dissolve the iodide in water, if possible, and determine the amount of iodine in it approximately, in the manner described below (*Analytical Process*); dilute the rest of the solution until it contains 1 part of iodine in about 1000 parts, and then determine the exact amount of iodine in it by the same method.

Should the iodide be insoluble in water, or not well adapted for direct solution, on account of foreign admixtures, distil with concentrated sulphuric acid, in a retort with the neck directed upwards, and continue the application of heat until sulphuric acid fumes begin to be evolved. Take care to add at first from 20 to 100 c.c. of fluid, 20 c.c. of sulphuric acid (free from iodine). Should the distillate contain free iodine with hydriodic acid, add 1 or 2 drops of thin starch-paste,* then aqueous solution of sulphurous acid, until the blue coloration is just disappearing. If the distillate contains sulphurous acid (as is the case, for instance, when urine containing iodine is distilled with sulphuric acid), add 1 or 2 drops of starch paste, and then, cautiously, solution of chloride of lime until the fluid just begins to show a blue tint, and dispel the blue coloration again by adding 1 or 2 drops of a weak aqueous solution of sulphurous acid. If the solution contains a very large amount of free acids, neutralize the latter partly with solution of soda.

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* This substance is not injured by the operation.

The Analytical Process.

Pour 10 c.c. of the solution of protochloride of palladium into a white glass flask, of from 100 to 200 c.c. capacity, dilute slightly with water, insert the cork loosely, and place the flask in a water-bath of from 140° to 212° F. Add now solution of iodide of potassium from the burette, shake, and heat a few seconds. When the fluid has cleared, which does not take long, pour some of it into 2 test tubes sufficient to fill them respectively to the height of 2 inches. By dropping some more solution of iodide of potassium into the one, and then comparing it with the other, you can readily see whether or not the iodide of potassium continues to produce a brown color in the fluid. Add now some more of the solution of iodide of potassium to the fluid in the flask, return to it also the sample from the test tubes, shake the flask, heat a few seconds, allow the fluid to become clear, test it again in the way just now described, and repeat the same process until further addition of iodide of potassium ceases to produce a coloration in the fluid. Now filter off a sample of the fluid, and test it both with protochloride of palladium and iodide of potassium; if neither produce a perceptible brown coloration, the experiment is at an end. It will be readily understood that, should too much iodide of potassium have been added, this error must be rectified by a further addition of 1 c.c. of solution of palladium.

The preliminary determination of the exact strength of the palladium solution is effected precisely in the same manner. Every 100 c.c. used of the solution of iodide of potassium (containing 0·100 of iodine) correspond to 0·042 grm. of palladium.

According to *Kersting's* experiments, the following bodies exercise no adverse influence on the process:—dilute hydrochloric acid, sulphuric acid, phosphoric acid, nitric acid, acetic acid, and the neutral salts of these acids with potassa, soda, and ammonia; also chloride of calcium and chloride of zinc; acetate of lead; sugar; uric acid and the distillate of urine with sulphuric acid; alcohol and ether; starch-paste; oil of lemon; also bromide of sodium, in presence of free acetic acid. The following bodies exercise an adverse influence on the process: bromide of sodium, in presence of free mineral acids, more especially upon heating; free alkalies; free chlorine, bromine, iodine, cyanogen; a large quantity of nitric acid, at a high temperature; sulphurous acid. These substances dissolve iodide of palladium, and consequently prevent the precipitation. This method of *Kersting's* has been tested in my own laboratory, and found to give very accurate results.*

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* *Kersting* prepares this by boiling 1 part of starch and 0·1 part of sulphuric acid in 24 parts of water.

d. A. and *F. Dupré's* method ("Annal. d. Chem. u. Pharm.," 94, 365). This is based upon the same principle as *Golfier-Besseyre's* method (*Schwarz*, "Anleitung zur Maassanalyse," 1853, page 114), viz., upon the circumstance that, when chlorine water or solution of chloride of soda (Na O Cl O) is added to a metallic iodide, the first equivalent of chlorine liberates iodine, which then combines with 5 more equivalents of chlorine to pentachloride of iodine. *Golfier-Besseyre* uses starch-paste in the process, whilst *A.* and *F. Dupré* employ, with much better success, chloroform or bisulphide of carbon, as these two substances are colored intensely violet by free iodine as well as by all compounds of iodine with chlorine containing less than 5 equivalents of chlorine.

The process may be conducted in two different ways.

a. Add chlorine water to a few litres of water, and determine the chlorine in the fluid as directed in § 142.

Take now of the fluid under examination a quantity containing no more than about 10 milligrammes of iodine, and pour this into a stoppered bottle, add a few grammes of pure chloroform or pure bisulphide of carbon (free from sulphur and sulphuretted hydrogen), and then gradually, drop by drop, chlorine solution, with an occasional vigorous shake of the bottle, until the violet color of the chloroform or sulphide of carbon just disappears; which point may be hit with the greatest precision. 6 equivalents of chlorine consumed in this process correspond to 1 equivalent of iodine. A still simpler way is to fix the strength of the dilute chlorine water by making it act, first upon a known quantity of iodide of potassium, say 10 c.c. of a solution containing 0·001 grm. of iodine in 1 c.c. (see § 145, *c*, *a*), then upon the fluid under examination. The amount of chlorine consumed in the first experiment is, in that case, to the known amount of iodine as the quantity consumed in the second experiment is to x.

In cases where the quantity of iodine is so considerable that sufficient of it is liberated upon the mere addition of chlorine water to impart a distinctly perceptible coloration to the fluid, it is better to delay adding the chloroform or bisulphide of carbon, until the color first produced has nearly disappeared again upon further addition of chlorine water.

That this method cannot be employed in presence of substances liable to be acted upon by free chlorine or iodine, is self-evident; organic matters, more particularly, must not be present. If they are, as is usually the case with mother liquors, the method *β.* should be employed.

β. Add to the fluid under examination chloroform or bisulphide of carbon, then chlorine water of unknown strength, until the fluid is *just* decolorized. At this point all the iodine is converted into $I\,Cl_5$. Add now solution of iodide of potassium in moderate excess; this will produce for every equivalent of $I\,Cl_5$, 6 equivalents of free iodine, which remains dissolved in the fluid. Determine the liberated iodine as directed in § 146, and divide the quantity found by 6: the quotient expresses the quantity of iodine contained in the examined fluid.

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* For *Herapath's* colorimetrical method, based upon the Palladium reaction, see "Phil. Mag.," Sept., 1853, p. 183.

In presence of metallic bromides, *Dupré's* method requires certain modifications, for which I refer to § 169.

This method is suited more particularly for the estimation of minute quantities of iodine. The results are most accurate.*

e. Duflos' method, based upon the separation of iodine from hydriodic acid or metallic iodides by distillation with sesquichloride of iron.

When hydriodic acid or a metallic iodide is heated, in a flask, with solution of pure sesquichloride of iron, the whole of the iodine escapes along with the aqueous vapour, and protochloride of iron is formed ($Fe_2\,Cl_3 + I\,H = Fe_2\,Cl_2 + Cl\,H + I$). The iodine passing over is received either in solution of iodide of potassium, or in a measured quantity of a solution of arsenite of soda of known strength, and its quantity determined as directed § 146.

Schwarz ("Anleitung zur Maassanalyse, Supplement," 1853, page 20) recommends, by way of control, to determine with solution of permanganate of potassa, the protochloride of iron in the residue in the flask; 2 equivalents of iron found in the state of protochloride correspond to 1 equivalent of iodine. The sesquichloride of iron used in the process must be free from chlorine, nitric acid, and protochloride. The best way is to prepare it with sesquioxide of iron and hydrochloric acid. The tube which conducts the iodine vapour into the receiving fluid need not dip into it.

Moride's method of separating iodine will be found in § 169.

II. *Separation of Iodine from the Metals.*

The metallic iodides are analysed like the corresponding chlorides. From iodides of the alkali metals containing free alkali the iodine may be precipitated as iodide of silver, by first saturating the free alkali almost completely with nitric acid, then adding solution of nitrate of silver in excess, and finally nitric acid to strongly acid reaction. If an excess of acid were added at the beginning, free iodine might separate, which is not converted completely into iodide of silver by solution of nitrate of silver.

With respect to the salts insoluble in water, I have to observe that many of them are more advantageously decomposed by boiling with potassa or soda, than by solution in dilute nitric acid, the latter process being apt to be attended with separation of iodine. This applies more particularly to protiodide of palladium, and to subiodide of copper and subiodide of mercury. From iodides soluble in water, the iodine may also be precipitated as protiodide of palladium.

Lastly, the base may be determined in one portion of the compound, by heating with concentrated sulphuric acid, the iodine, in another portion, by the method I., *e.*

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* *Luca* ("Compt. rend.," 37, 866; "Journ. f. prakt. Chem.," 61, 137) recommends another method, based upon the same principle as *Dupré's*. Instead of chlorine water, he uses a solution of bromine of known strength; the process is terminated when further addition of bromine water fails to impart a color to newly added chloroform. This method is not so convenient and practical as *Dupré's*. Compare also *Casaseca* ("Annal. de Chim. et Phys.," 45, 482; *Liebig* and *Kopp's* "Ann. Rep.," 1855, 790.)

Supplement.

Determination of Free Iodine.

§ 146.

1. *Bunsen's* method ("Annal. d. Chem. u. Pharm.," 86, 265).

a. Principle of the Method.—The theory of this simple, neat, and accurate method, upon which a number of analytical processes are founded, is as follows :

α. Iodine and sulphurous acid decompose in presence of water to hydriodic acid and sulphuric acid ($I + HO + SO_2 = HI + SO_3$) ; but, on the other hand, sulphuric acid and hydriodic acid are decomposed again into iodine, sulphurous acid, and water ($HI + SO_3 = I + HO + SO_2$). Which of these two reactions will ensue or prevail, depends upon the relative degrees of concentration of the solution. Now, *Bunsen* has ascertained, by most careful experiments, that, when iodine is brought into contact with an aqueous solution of sulphurous acid containing no more than from 0·04 to 0·05 per cent. by weight of anhydrous acid, the first reaction alone takes place ; under these circumstances, therefore, 1 equivalent of iodine converts 1 equivalent of sulphurous acid into sulphuric acid.

β. If therefore an unknown quantity of iodine, dissolved in iodide of potassium, is mixed with an excess of such highly dilute sulphurous acid of known strength, and the amount of the sulphurous acid remaining in that form then determined, the difference shows at once the amount converted into sulphuric acid, and hence also the amount of iodine.

γ. The strength of the dilute solution of sulphurous acid is determined by ascertaining how much of a solution of iodine of known strength is required to convert the sulphurous acid into sulphuric acid.

b. Materials required. It results from *a* that the following fluids are required for the analytical process :

α. *A Solution of Iodine* of known strength.—This is prepared by dissolving 5 grammes of the purest iodine—dried for some time under a bell glass over sulphuric acid and chloride of calcium—with the aid of a concentrated solution of pure iodide of potassium,* in a measuring flask holding 1 litre, adding water up to the litre mark, and shaking the flask until perfect intermixture has taken place. As 1000 c.c. of this solution contain accordingly 5 grammes of iodine, every c.c. contains 0·005 grm. of iodine. But as iodine mostly contains traces of chlorine, which latter agent acts upon sulphurous acid the same way as iodine, but has a different equivalent, the solution must be tested to ascertain how much absolutely pure iodine corresponds to one cubic centimetre of the iodine solution in its action upon sulphurous acid.

This examination will be found in *c. β.*

β. *A Solution of Sulphurous Acid.*—Saturate water completely with sulphurous acid, at the common temperature, pour the solution into bottles, close the latter tight, and place them inverted in water. Add from 35 to 40 c.c. of this saturated solution to 5000 c.c. of water.

γ. *A Solution of Iodide of Potassium.*—Dissolve 1 part by weight of pure iodide of potassium (free from iodic acid) in about 10 parts by weight of water. The solution must show no brown tint, neither upon standing in the air, nor immediately after addition of hydrochloric acid.

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* This solution must be colorless, and must show no brown coloration immediately after addition of hydrochloric acid.

δ. *Starch-paste.*—This should be prepared fresh for every new experiment; it must be very thin and almost perfectly clear.

c. *Preliminary Determinations.*

a. *Determination of the relative strength of the Solution of Iodine and the Solution of Sulphurous Acid.*

Measure, by means of a pipette, 50 c.c. of the dilute solution of sulphurous acid, and transfer to a flask. Add 3 or 4 c.c. of starch paste, and then the solution of iodine drop by drop, from a burette,* well stirring until the coloration produced by the last drop just remains permanent.

Suppose you have used 12·5 c.c. of iodine solution to 50 c.c. of the solution of sulphurous acid, then

$$50 : 12·5$$

will indeed *approximately* express the relative strength of the iodine solution and the sulphurous acid, but by no means with the degree of accuracy attainable by a second experiment, which is made as follows:—Transfer about 24 c.c. of solution of iodine from a pipette to a flask, and add 100 c.c. of the solution of sulphurous acid, which will just cause the yellow color to disappear; add 3 or 4 c.c. of starch-paste, and then, with great care, some more iodine solution, until the coloration produced by the last drop just remains permanent. By now reading off the total quantity of iodine solution consumed, the relative strength of this and the sulphurous acid is learnt with the greatest accuracy. The prompt addition of the sulphurous acid solution to the iodine solution, in this second experiment, effectively prevents alteration of the former by evaporation or atmospheric action.

Suppose you have found the corresponding proportion between the iodine solution and sulphurous acid solution to be, 26 c.c. of the former to 100 c.c. of the latter.

As the sulphurous acid solution suffers alteration from the oxidizing action of the air, this preliminary determination must be repeated before every fresh series of experiments.

β. *Determination of the exact amount of iodine in the iodine solution* (or, more correctly, determination of the action of the iodine solution upon sulphurous acid, &c., expressed in parts by weight of pure iodine).

As the correct determination of the strength of the iodine solution is the foundation on which this analytical method rests, the greatest care must be bestowed on this part of the process. Of the various methods by which the intended end may be attained, I will describe four, all of which give very accurate results.

aa. *Determination of the Strength of the Iodine Solution by means of Pure Iodine.*

Select three well fitting watch-glasses, *a*, *b*, and *c*; weigh *b* and *c* together accurately. Put about 0·5 grm. of pure dry iodine, prepared according to the direction of § 65, 5, into *a*; place the latter, with its contents, on a small piece of sheet iron, and heat gently, until thick fumes of iodine escape. Cover *a* now with *b*, and regulate the action of the heat so that the iodine will entirely, or almost entirely, sublime in *b*. Now remove *b*, whilst still hot, give it a gentle swing in the air, to remove the still uncondensed iodine fumes and traces of aqueous vapor, cover with *c*, place under the desiccator till cold, weigh, and transfer the two watch-glasses, together with the weighed iodine, to a capacious beaker, containing a sufficient quantity of iodide of potassium solution to dissolve the whole of the iodine to a clear fluid. Add to the solution one 50 c.c. pipette after another of your sulphurous acid, until the fluid appears quite colorless after the addition of the last pipette. Suppose the weight of the iodine in *b* was 0·3 grm. (after the deduction of the tare of the two glasses *b* and *c*), and you have used 5 pipettes = 250 c.c. of sulphurous acid solution to effect complete decolorization.

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* One with caoutchouc connector and clamp answers the purpose best.

Now add to the colorless fluid 3 or 4 c.c. of starch solution, and then solution of iodine* from the burette, until the last drop just produces a permanent blue color. Suppose this takes 5 c.c. of iodine solution. The calculation is now exceedingly simple, as the following short illustration will show, which is based upon the quantities supposed to have been found in the preceding experiments :—

100 c.c. of sulphurous acid solution correspond to 26 c.c. of iodine solution, 250 c.c. accordingly to 65 c.c. Deducting from these 65 c.c. the number of cubic centimetres of iodine solution added in the last experiment to effect the conversion of the excess of the sulphurous acid into sulphuric acid—viz., 5 c.c., we find that 60 c.c. of the iodine solution have the same power of action as the weighed quantity of pure iodine used in the experiment preceding—viz., 0·3 grm. Each cubic centimetre of the iodine solution corresponds, accordingly, to 0·005 grm. of pure iodine.

I prefer this method to all others, as being the most practical and convenient, and giving the most accurate results. It has this great advantage over the method originally proposed by *Bunsen* (see *bb.*), that the results obtained by it are not liable to be vitiated by a possible error in the assumed equivalent number of one of the determining elements in it.

bb. Determination of the Strength of the Iodine Solution by means of Bichromate of Potassa.

This is the method originally proposed by *Bunsen*. It agrees in the essential points with *aa*, with this difference, however, that, instead of the iodine being weighed, a determinate quantity is liberated by conducting into a solution of iodide of potassium a known amount of chlorine, produced by heating a weighed quantity of bichromate of potassa with hydrochloric acid.

Weigh about 0·35 grm. of pure bichromate of potassa, rendered perfectly anhydrous by fusion at a gentle heat, and treat with pure fuming hydrochloric acid, in the manner directed in § 130, *d*, *β*. When quite cold, transfer the fluid to a beaker, and proceed exactly as in *aa*. 1 equivalent of $KO, 2\,CrO_3$ (148·67) corresponds to 3 equivalents of iodine (380·64).

With proper care, this method answers very well, but it requires a more skilful manipulation than *aa*. It presents, also, this great disadvantage, that, as chemists are not yet agreed on the correct equivalent of chromium, one of the principal elements on which rests the correctness of the results is uncertain, and may possibly be false.

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* That is to say, the iodine solution, of which the exact strength is to be determined, the corresponding proportion which it bears to the sulphurous acid solution having been ascertained already in *a*.

cc. Determination of the Strength of the Iodine Solution by means of Arsenious Acid.

This method is based upon the principle explained in section 127, 5.

Prepare an arsenite of soda solution of accurately known strength, in the manner directed in § 142, 1, *b*, by dissolving about 0·5 grm. to the volume of 250 c.c., transfer 50 c.c. of the solution to a beaker, add from 10 to 20 c.c. of a cold saturated solution of bicarbonate of soda, then a little starch-paste, and finally solution of iodine, until the blue color of the iodized starch just begins to appear. 1 equivalent of arsenious acid (99·00) corresponds to 2 equivalents of iodine (253·76). This method, proposed and warmly recommended by *Fr. Mohr*, gives also satisfactory results.

dd. Determination of the Strength of the Iodine Solution by means of Hyposulphite of Soda.

See § 146, 3.

The iodine solution should be kept in small bottles, with well-fitting ground glass stoppers, in the cellar. By means of a correct determined standard solution of iodine, the strength of other iodine solutions, prepared at some after period, may always readily be determined, by simply establishing the respective power of action of the two upon equal quantities of the same solution of sulphurous acid.

d. The process.

Weigh the iodine, best in a small flask, dissolve in the iodide of potassium solution prepared after *b*. γ. (using about 5 c.c. of iodide of potassium solution to 0·1 grm. of iodine), add one pipette after another of the sulphurous acid solution, until the fluid appears quite colorless after the addition of the last pipette. Now add starch-paste, and, finally, graduated solution of iodine from the burette, until the final reaction is attained.

Calculate the number of cubic centimetres of iodine solution corresponding to the sulphurous acid consumed in the experiment, and deduct from this the number of c.c. used to effect the conversion of the excess of the sulphurous acid into sulphuric acid. The difference expresses the number of cubic centimetres of iodine solution, containing exactly the same quantity of iodine as the examined sample. To know the amount of iodine in the latter, therefore, you need simply multiply the number of cubic centimetres with the known amount of iodine in 1 c.c.

As the measuring of the sulphurous acid with the pipette, or measuring flask, is rather a tedious operation, the following apparatus may be advantageously employed in laboratories where determinations of iodine by *Bunsen's* method are of frequent occurrence.

A is a large bottle, say of 10 litres capacity. Fill this nearly with water; add from 70 to 80 cubic centimetres of a saturated solution of sulphurous acid, shake the mixture vigorously, and place the bottle on a raised firmly-fixed stand. Join *h* to *f* and *g*, by means of the vulcanized india-rubber tube *e*, and push the end of the caoutchouc tube, which projects below the compression clamp *a*, over the little tube opening into *c d*; the end of this tube is bent sideways, by which arrangement the liquid passing through it is made to flow quietly down the side of *c d*. The tube *g* contains small lumps of phosphorus interspersed between pieces of asbestos; *f* contains hydrate of potassa. The tube *c d* is perpendicularly fixed, by means of two iron rings (not marked in the engraving), or in some other way, to the wall, or to a proper stand, with 10 or 12 centimetres clear space between, and the *o* point on a level with the eye of the operator. This tube is accurately graduated from above downward for delivering the volumes marked in it; there is no need of making the divisions smaller than 50 cubic centimetres each. To graduate the tube, fill it with water up to the zero mark and allow 50 c.c. to flow out through *b*, into a measuring tube accurately graduated for holding the volumes marked on it (or 50 grm. of 39·2° F., or 49·95 grm. of 60·8° F., into a tared flask), and then mark the height of the fluid remaining in the tube by cutting a line with a diamond; repeat the same operation until the tube is graduated in its whole length.

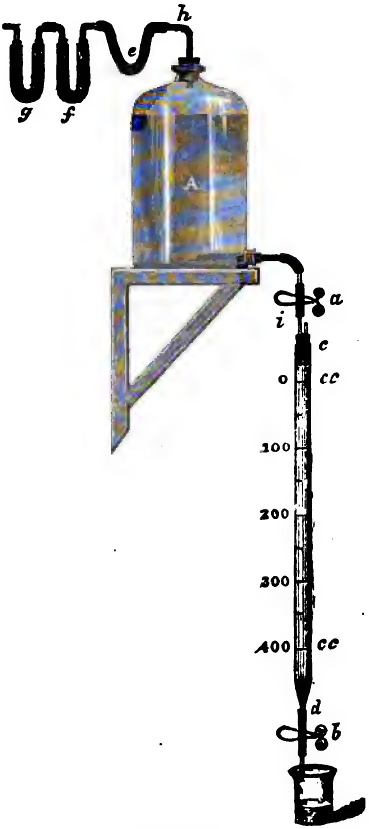

Fig. 72.

The mode of using this apparatus is self-evident. When the tube *c d* is to be filled from A, the compression clamp *a* is opened; when a measured quantity of sulphurous acid is required, the compression clamp *b*. The fluid drawn through *b* is allowed to flow gently down the side of the beaker.

2. *With Arsenite of Soda and Iodine Solution. Fr. Mohr's* method, slightly modified.

The process requires a standard iodine solution, prepared as directed in 1 (*Bunsen's* method), and a solution of arsenite of soda prepared as directed § 142, 1, *b*. The relative proportion between the two is fixed according to the directions given in the same place. The sample under examination is mixed with a measured quantity of the solution of arsenite of soda, which must be slightly in excess; starch-paste is then added, and also bicarbonate of soda, and the excess of arsenious acid determined by means of the iodine solution. If the amount consumed to oxidize the excess of the arsenious acid is deducted from the quantity of iodine solution corresponding to the arsenious acid, the difference expresses the number of cubic centimetres of iodine solution containing exactly the same amount of iodine as the examined sample, and accordingly gives also the weight of the iodine to be determined.

3. *With Hyposulphite of Soda* (*Schwarz's* method, "Anleitung zur Maassanalyse, Supplement," 1853, page 22). This method is based upon the following reaction: $2\ (Na\,O,\ S_2\,O_2) + I = Na\,I + Na\,O,\ S_4\,O_5$. 24·84 grammes of pure crystallized hyposulphite of soda are dissolved to the volume of 1 litre. 100 c.c. of the solution correspond to 1·2688, *i.e.*, to 00·1 equivalent of iodine. This solution (which according to *Fr. Mohr*[*] retains its strength, or standard, unaltered) is added to the solution of the sample in iodide of potassium, until the fluid appears of a bright yellow, thin and very clear starch-paste is then added, which must produce blue coloration, and finally again hyposulphite of soda, until the blue fluid is just again decolorized. According to *Fr. Mohr*, this method gives very accurate results.

If a fluid contains free iodine in presence of iodine in a state of combination, the former is determined in one portion of the fluid, by either of the preceding methods (1, 2, or 3), and the total amount of iodine present in another portion of the fluid. To this end, sulphurous acid is added until the fluid appears colorless, and then solution of nitrate of silver (145, *a*); the precipitate is digested with nitric acid, to remove any sulphate of silver that might have been thrown down along with it, filtered, &c.; or the fluid is distilled with sesquichloride of iron, as directed in § 145, *e*.

§ 147.

4. HYDROCYANIC ACID.

I. *Determination.*

a. If you have free hydrocyanic acid in solution, mix the solution, in a rather dilute state, with solution of nitrate of silver in excess, add a little nitric acid, and determine the precipitated cyanide of silver as directed in § 115, 3.

If you wish to determine in this way the hydrocyanic acid in bitter almond water or cherry laurel water, add ammonia after the addition of the solution of nitrate of silver, and then supersaturate slightly with nitric acid. This modification of the process is indispensable to precipitate from these fluids the whole of the hydrocyanic acid as cyanide of silver.

b. Liebig's Volumetrical Method ("Annal. der Chem. und Pharm.," 77, 102).—If hydrocyanic acid is mixed with potassa to strong alkaline reaction, and a dilute solution of nitrate of silver is then added, a permanent precipitate of cyanide of silver—or, if a few drops of solution of chloride of sodium have been added (which is always advisable), of chloride of silver—forms only after the whole of the cyanogen is converted into double cyanide of silver and potassium. The first drop of solution of nitrate of silver added in excess produces the permanent precipitate. 1 equivalent of silver consumed in the process corresponds, therefore, exactly to 2 equivalents of hydrocyanic acid ($2\ K\,Cy + Ag\,O,\ NO_5 = Ag\,Cy,\ K\,Cy + K\,O,\ N\,O_5$). A decimal solution of nitrate of silver, containing 10·797 grammes of silver in the litre, should be used; 1 c.c. of this solution corresponds to 0·0054 of hydrocyanic acid. In examining medicinal hydrocyanic acid, 5 to 10 grammes ought to be used, but of bitter almond water about 50 grammes; if exactly 5·4 or 54 grammes are used, the number of cubic centimetres consumed of the silver solution, divided by 10, or by 100, expresses exactly the percentage amount of hydrocyanic acid contained in the examined sample. Medicinal

[*] *Fr. Mohr's* "Lehrbuch der Titrirmethode." Addition to page 332.

hydrocyanic acid is suitably diluted first by adding from 5 to 8 volumes of water; bitter almond water also, is slightly diluted; if turbid, acohol is added until the turbidity disappears.

Liebig has examined by this method hydrocyanic acid of various degrees of dilution, and has obtained results corresponding exactly with those obtained by *a.* In this method it does not matter whether the hydrocyanic acid contains an admixture of hydrochloric acid or formic acid. A considerable excess of potassa must be avoided.

If it is intended to determine cyanide of potassium by this method, a solution of that salt must be prepared of known strength, and a measured quantity used containing about 0·1 grm. of the salt. Should it be mixed with sulphide of potassium, it is first freed from this, by adding a few drops of a solution of a salt of cadmium, and filtering off the precipitated sulphide of cadmium.

c. Fordos and *Gelis's Volumetrical Method*[*] ("Journ. de Chim. et de Pharm.," 23, 48. "Journ. f. prakt. Chem.," 59, 255).—This method is founded upon the reaction of free iodine upon cyanide of potassium:[†] $K\,Cy + 2\,I = K\,I + I\,Cy$. 2 equivalents of iodine = 253·76 correspond accordingly to 1 equivalent of cyanogen = 26, or to 1 equivalent of hydrocyanic acid = 27, or to 1 equivalent of cyanide of potassium = 65·11.

The iodine solution is prepared according to the directions of § 146. If you have to examine free hydrocyanic acid, mix the fluid cautiously with solution of soda to alkaline reaction, add water containing carbonic acid (Selters or soda water), to convert a possible excess of alkali into bicarbonate, and then iodine solution, until a permanent yellow color is produced. For the analysis of cyanide of potassium, prepare a fluid of known strength, and use a volume containing 0·05 of cyanide of potassium; addition of carbonic acid water is necessary in the process. The cyanide must contain no sulphide of potassium. The method gives satisfactory results.

d. C. Mohr's Method.—For the principle of this method, see § 119, 4, *d.* As the decomposition is not uniformly the same, I cannot recommend the method.

II. *Separation of Cyanogen from the Metals.*

a. In soluble Metallic Cyanides (cyanide of mercury excepted).

Mix the solution of the cyanide with solution of nitrate of silver in excess, add nitric acid to acid reaction, and proceed as in I., *a.* Determine the bases in the filtrate, after the removal of the excess of the salt of silver added; see Section V.

b. In insoluble Metallic Cyanides which dissolve readily in dilute Nitric Acid.

Dissolve the cyanide by shaking with extremely dilute nitric acid, in a stoppered flask, add nitrate of silver in excess, and proceed as in II., *a.*

c. In all Cyanides from which the Cyanogen may be completely expelled by heating with Hydrochloric Acid.

Heat the cyanide with water, in a small distillation flask, having a burette (with caoutchouc connector and compression clamp) inserted through the cork. Let hydrochloric acid flow in in small portions, by opening the clamp, until the fluid in the flask contains a strong excess of acid. Fit the tubulated receiver air-tight to the apparatus, and connect the tubulature, by means of a limbed tube, with a U-shaped tube. The latter and the receiver contain a little solution of soda. After the termination of the process, treat the contents of the receiver and U tube as directed I., *b.*

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[*] With regard to *Herapath's* colorization method, which is founded on the intensity of the color of a sulphurous oxide of iron solution, compare "Journ. f. prakt. Chem.," 60, 242; "Phil. Mag.," Sept., 1853, vol. vi. p. 185.

[†] Mentioned first by *Serullas* and *Wöhler*.

d. In all insoluble Metallic Cyanides.

Ignite the cyanide, and determine the metal in the residue, either by direct weighing, or by solution in acid and precipitation. The amount of cyanogen is either inferred from the loss, or determined by the method of organic analysis. Many of the metallic cyanides may be decomposed also by evaporation with hydrochloric acid, or by boiling with oxide of mercury. In the latter case, the oxides separate, mixed with the excess of the oxide of mercury, whilst basic cyanide of mercury dissolves.

e. In Cyanide of Mercury.

Precipitate the aqueous solution with sulphuretted hydrogen, and determine the mercury as directed in § 118, 3, and the hydrocyanic acid formed as directed in § 169.

The cyanogen may be advantageously determined, also, in a separate portion by the method of the qualitative determination of nitrogen (§ 184).

III. *Analysis of Double Protocyanides* (Ferrocyanides, &c.).

a. Volumetric Determination of Ferro- and Ferricyanogen.

This method devised by one of the students in my laboratory, Mr. *E. de Haen*, is founded upon the simple fact that a solution of ferrocyanide of potassium acidified with hydrochloric acid (which may accordingly be assumed to contain free hydroferrocyanic acid), is by addition of permanganate of potassa converted into the corresponding ferricyanide. If this conversion is effected in a very dilute fluid, containing about 0·2 grm. of ferrocyanide of potassium in a volume of from 200 to 300 cubic centimetres, the termination of the reaction is clearly and unmistakably indicated by the change of the originally pure yellow color of the fluid to reddish-yellow.

The process requires two test fluids of known strength, viz.,

1. A solution of pure ferrocyanide of potassium.
2. A solution of permanganate of potassa.

The *former* is prepared by dissolving 20 grammes of perfectly pure and dry crystallized ferrocyanide of potassium in the necessary quantity of water to give 1 litre of solution; each c.c. of this solution therefore contains 20 milligrammes of ferrocyanide of potassium. The *latter* is diluted to the extent that somewhat less than a burette full is required for 10 c.c. of the solution of ferrocyanide of potassium.

To determine the strength of the permanganate of potassa solution in its action upon ferrocyanide of potassium, measure off, by means of a small pipette, 10 c.c. of the solution of ferrocyanide of potassium (containing 0·200 grm.) dilute with about 250 c.c. of water, acidify with hydrochloric acid, place the glass on a sheet of white paper, and allow the solution of permanganate of potassa to drop into the fluid, stirring it at the same time, until the change from yellow to *reddish*-yellow indicates that the conversion is complete.[*] Repetitions of the experiment always give very accurately corresponding results. As the solution of permanganate of potassa is liable to alteration, its strength must always be determined before every new series of experiments.

To determine the amount of ferrocyanide of potassium contained in any given sample of the yellow salt of commerce, dissolve 5 grammes of the latter in the necessary quantity of water to give 250 c.c. of solution; take 10 c.c. of this solution, and examine as just now directed. Suppose, in determining the strength of the solution of permanganate of potassa in its action upon ferrocyanide of potassium, you have used 20 c.c., and you find now that 19 c.c. is sufficient, a simple calculation,

$$20 : 0{\cdot}200 :: 19 : x$$

will inform you how much pure ferrocyanide of potassium the analysed salt contains. And even this may be dispensed with, by diluting the solution of permanganate of potassa so that exactly 50 c.c. correspond to 0·200 of ferrocyanide of potassium, as, in that case, the number of half-cubic centimetres consumed expresses directly the percentage amount of the ferrocyanide of potassium present in the analysed salt.

Instead of determining the strength of the permanganate of potassa solution by means of pure ferrocyanide of potassium, which is unquestionably the best way, one of the methods given in § 112, 2 may also be employed; bearing in mind, in that case, that 2 equivalents of ferrocyanide of potassium = 422·44 (together with the water of crystallisation), 2 equivalents of iron dissolved to protoxide = 56, and 1 equivalent of oxalic acid = 63 (together with the water of hydration and crystallisation) are equivalent in their action upon solution of permanganate of potassa.

The analysis of soluble ferricyanides by this method is effected by reducing them to ferrocyanides, acidifying, and then proceeding in the same way as just now described. The reduction is effected as follows:—Mix the weighed ferricyanide with solution of soda or potassa in excess, boil, and add concentrated solution of sulphate of protoxide of iron gradually, and in small portions, until the color of the precipitate appears black, which is a sign that protosesquioxide of iron has precipitated. Dilute now to the volume of 300 cubic centimetres, and proceed to determine the ferrocyanide in portions of 50 or 100 c.c. of the fluid. As the space occupied by the precipitate is not taken into account in this process, the results are not absolutely accurate. The difference is so very trifling, however, that it may safely be disregarded.

Insoluble ferro- or ferricyanides, decomposable by boiling solution of potassa (as are most of these compounds), are analysed by boiling a weighed sample sufficiently long with an excess of solution of potassa (adding, in presence of ferricyanides, sulphate of protoxide of iron), and then proceeding in the same way as directed above.

Ferricyanides may be analysed also by another method, also devised by one of the students in my laboratory, Mr. *E. Lenssen.* It is founded on the fact that, when ferricyanide of potassium, solution of iodide of potassium, and concentrated hydrochloric acid are mixed together, 1 equivalent of iodine = 126·88 separates for every equivalent of ferricyanide of potassium $= 329{\cdot}5$ $(\mathrm{Cfdy}, H_3) + IH = 2\ (\mathrm{Cfy}\ H_2) + I.$

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[*] If you wish for some additional evidence besides the change of color, add to a drop of the mixture on a plate, a drop of solution of sesquichloride of iron: if this fails to produce a blue tint, the conversion is accomplished.

By determining the liberated iodine by *Bunsen's* method (§ 146), we learn the quantity of the ferricyanide of potassium. *Lenssen* obtained in 4 experiments respectively, 99·22,—101·7,—102·1,—100·5, instead of 100.

b. Methods based upon the Destruction of the Cyanogen.

a. Bolley's method ("Annal. d. Chem. u. Pharm.," 87, 254).

Mix a weighed sample of the dried double cyanide with 3 or 4 times the quantity of a mixture of 3 parts of sulphate and 1 part of nitrate of ammonia; transfer the powder to a small tubulated retort, rinse the mortar, &c., with the mixture of the two ammonia salts, add the rinsings to the powder in the retort, join a receiver loosely to the neck of the latter, and heat over a spirit-lamp, shaking the mixture occasionally. Complete decomposition ensues even at a moderate heat, attended with glimmering of the mass; the whole of the cyanogen volatilizes in the form of cyanide of ammonium and of the products of the decomposition of the latter substance, whilst the metals remain as sulphates. As traces of these may have been carried over into the receiver, evaporate the fluid contained in the latter in a porcelain dish, volatilize the ammonia salts (if necessary), and dissolve what remains in the receiver in a little nitric acid. Dissolve the residue in the retort in water, adding, if necessary, some nitric acid, and then separate the metals in the clear solution by the appropriate methods, which are given in Section V. *Bolley* says he obtained very accurate results by this simple and easy method, in the decomposition of various ferro- and ferricyanides.

β. Claus (Jahresbericht v. *Liebig* and *Kopp*, 1855, 816) recommends to decompose the double protocyanide of platinum and the alkali metals by heating a mixture of 1 part of the salt with 4 parts of nitrate of suboxide of mercury, in small portions, in a platinum crucible. The mass deflagrates feebly; the platinum and alkali are easily determined in the residue, after volatilization of the oxide of mercury.

γ. The estimation of the nitrogen and carbon (cyanogen) in such compounds is effected by the methods given in Section VI. (Ultimate or Elementary Analysis of Organic Bodies).

c. Determination of the Alkalies, more particularly of Ammonia in soluble Ferrocyanides.

Mix the boiling solution with solution of chloride of copper in moderate excess, filter the precipitated ferrocyanide of copper, free the filtrate from copper by sulphuretted hydrogen, and then determine the alkalies (*Reindel*, "Journ. f. prakt. Chem.," 65, 452).

§ 148.

5. HYDROSULPHURIC ACID (Sulphuretted Hydrogen).

I. *Determination.*

Sulphuretted hydrogen in the free state is most readily and very accurately determined by volumetric analysis, by means of iodine; the sulphur in it may also be determined by converting it into a suitable sulphide or into sulphate of baryta, and weighing.

a. The method of determining free sulphuretted hydrogen by volumetric analysis, by means of a solution of iodine, was employed first by *Dupasquier*. That chemist used alcoholic solution of iodine for the purpose. But as the action of the iodine upon the alcohol gradually alters the composition of this solution, it is better to use a solution of iodine in iodide of potassium. The decomposition ensues according to the formula:

$$HS + I = HI + S$$

1 equivalent of I = 126·88 corresponds to 1 equivalent of HS = 17. However, this exact decomposition can be relied upon with certainty only if the amount of sulphuretted hydrogen in the fluid to be analysed does not exceed 0·04 per cent. (*Bunsen*). Fluids containing a larger proportion of sulphuretted hydrogen must therefore first be diluted to the required degree with boiled water free from air, and cooled out of the contact of air.

The iodine solution of § 146 may be used for the estimation of larger quantities of sulphuretted hydrogen; for weak solutions, *e.g.* sulphuretted mineral water, it is advisable to dilute the iodine solution of § 146 to 5 times the volume, which accordingly will give a fluid containing about 0·001 grm. of iodine in the cubic centimetre.

The process is conducted as follows:—

Measure or weigh a certain quantity of the sulphuretted water, dilute, if required, to the proper degree with boiled water free from air, and cooled out of the contact of air, add some thin starch-paste, and then solution of iodine, with constant shaking or stirring, until the permanent blue color of iodized starch begins to appear. The result of this experiment indicates approximately, but not with positive accuracy, the relative or corresponding proportion between the examined water and the iodine solution. Suppose you have consumed, to 220 cubic centimetres of sulphuretted water, 12 cubic centimetres of a solution of iodine containing 0·000918 grm. of iodine in the cubic centimetre.* Introduce now into a flask nearly the quantity of iodine solution required, weigh, add sulphuretted water until the fluid is just decolorized, insert the stopper, and weigh again; then add starch-paste, and after this iodine solution until the blue color of iodized starch just begins to show. By this course of proceeding, you avoid the loss of sulphuretted hydrogen which would otherwise be caused by evaporation and oxidation. Instead of determining the quantity of the sulphuretted water by weight, it may be determined also, in a suitable way, by measure. In my analysis of the *Weilbach* water, 256 c.c. of the water required, in my second experiment, 16·20 c.c. of iodine solution, which, calculated upon the quantity of sulphuretted water used in the first experiment, viz, 220 c.c., makes 13·9 c.c., or 1·9 c.c., more than was used in the first experiment in which chance of loss by evaporation or oxidation had not been guarded against by the course of proceeding adopted in the second.

But even now the experiment cannot yet be considered quite conclusive, when made with a very dilute solution of iodine, as in the case given here by way of illustration; but it is still necessary to ascertain how much iodine solution is required to impart the same blue tint to the same quantity of a similar mixture of starch and ordinary water of the same temperature, and as nearly as possible the same state and condition as the analysed sulphuretted water (comp. "Annal. d. Chem. u. Pharm.," 102, 186), and to deduct this from the quantity of iodine solution used in the second experiment. Thus in my analysis of the *Weilbach* water, I had to deduct 0·5 c.c. from the 16·20 c.c. consumed in the second experiment. If the instructions here given are strictly followed, this method gives very accurate results (see Analytical Notes and Experiments, No. 86).

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* The numbers here stated are those which I obtained in the analysis of the *Weilbach* water.

b. Fr. Mohr's method slightly modified.

Mix the sulphuretted fluid with a slight excess of solution of arsenite of soda of known strength (determined by means of iodine solution, see § 142, *b*), and add hydrochloric acid to distinct acid reaction. Dilute to the volume of 300 cubic centimetres, pass through a dry filter, test a sample of the filtrate with sulphuretted hydrogen, to make quite sure that it still contains arsenious acid, and then determine in 100 c.c., after addition of powdered bicarbonate of soda, the remainder of the arsenious acid left in it. Deduct the quantity of iodine solution consumed in the last part of the process, multiplied by 3 (as only 100 of the 300 c.c. have been operated upon), from that which would have been required to effect the decomposition of the entire quantity of arsenious acid used in the process: the difference expresses the quantity of iodine solution corresponding to the sulphuretted hydrogen contained in the analysed fluid. In making the calculation, bear in mind that 2 equivalents of iodine will now correspond to 3 equivalents of $H S$, since 1 equivalent of $As O_3$ decomposes, on the one hand, $3 H S$ to $As S_3$ and $3 H O$, and requires, on the other hand, 2 equivalents of iodine for its conversion into arsenic acid.

Very dilute solutions of sulphuretted hydrogen cannot be analysed by this method, as the sulphide of arsenic separating from them takes a very long time to deposit, and a minute portion of it invariably remains in solution.*

c. Mix the hydrosulphuretted fluid with an excess of solution of arsenite of soda, add hydrochloric acid, let deposit, and determine the sulphide of arsenic as directed § 127. If the quantity of sulphuretted hydrogen in the analysed fluid is moderately large, the results obtained by this method are accurate (comp. Analytical Notes and Experiments, No. 86); but in the case of very dilute solutions, the results are too low, as a little tersulphide of arsenic remains in solution. In my analysis of the *Weilbach* water, this method gave, therefore, only 0·006621 and 0·006604 per mil., whilst *a* (Determination by Solution of Iodine) gave 0·007025 of $H S$ per mil. Instead of arsenious acid, solution of chloride of copper or of nitrate of silver may be employed as precipitant, and the sulphur determined in the sulphide of copper as sulphate of baryta (§ 148, II.), or in the sulphide of silver as chloride of silver. The results obtained by precipitating with chloride of copper are also too low, in the case of very dilute fluids. As regards precipitation by silver solution, I cannot yet speak from actual experience. *Lyte* ("Compt. rend.," 43, 765) recommends solution of chloride of silver in hyposulphite of soda, mixed with a few drops of ammonia, as the most suitable for the purpose.

For the analysis of mineral waters, the method *a* will always answer best, unless presence of hyposulphites should impair its accuracy.

d. If the sulphuretted hydrogen is evolved in the gaseous state, the best way is to conduct it first through several U-tubes, containing an alkaline solution of arsenite of soda, then through a tube connected with the exit-mouth of the last U-tube, which contains pieces of glass moistened with solution of soda; to mix the fluids afterwards, and proceed as in *b* or *c*.

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* A solution containing in the litre 0·003 $H S$ gave with a solution of arsenious acid in hydrochloric acid, only after twelve hours, a precipitate admitting of filtration.

II. *Separation and Determination of the Sulphur in Metallic Sulphides.*

1. *Methods in the Dry Way.*

a. In all Sulphides which lose no Sulphur by the Action of Heat.

Mix a weighed quantity of the pulverized substance with 3 parts of anhydrous carbonate of soda and 4 of nitrate of potassa, with the aid of a rounded glass rod, wipe the particles of the mixture which adhere to the rod, carefully off against some carbonate of soda, and add this to the mixture. Heat the latter in a platinum or porcelain crucible (which, however, is somewhat affected by the process), at a gradually increased temperature to fusion; keep the mass in that state for some time, then allow it to cool, heat the residue with water, filter, and determine in the filtrate, which contains the whole of the sulphur as alkaline sulphate, the sulphuric acid as directed in § 132. The metal, metallic oxide, or carbonate, which remains undissolved, is determined, according to circumstances, either by direct weighing or in some other suitable way.

b. In Metallic Sulphides which lose Sulphur by the Action of Heat.

Mix the finely pulverized compound with 4 parts of carbonate of soda, 8 of nitrate of potassa, and 24 of pure and perfectly dry chloride of sodium, and treat the mixture as in *a*. Or, mix the very finely pulverized substance with 3 parts of pure carbonate of soda and 3 of pure chlorate of potassa, put the mixture into a tube of difficultly fusible glass, sealed at one end, fill the fore part of this tube with carbonate of soda mixed with a little chlorate of potassa, and heat in a combustion furnace in the same way as in organic analysis. Treat the ignited saline mass as in *a*. The solution will, of course, contain silicic acid from the glass (*Kemp*).

c. In Sulphur Salts of more Complex Composition (Berzelius and H. Rose).

Use the apparatus illustrated by Fig. 73, or one of similar construction.

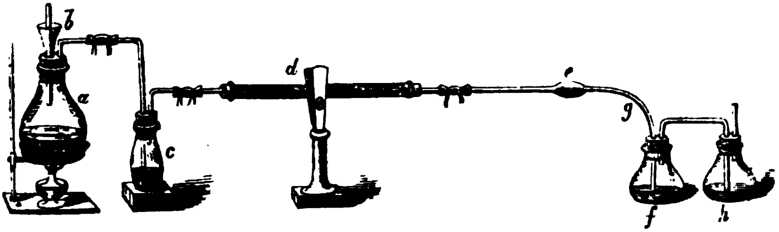

Fig. 73.

a is a flask from which a slow current of chlorine is evolved;* *b* serves to convey into *a* additional portions of hydrochloric acid; *c* contains concentrated sulphuric acid, *d* chloride of calcium—both intended for drying the chlorine evolved; *e* is a bulb-tube intended to receive the substance to be analysed; this tube reaches to near the surface of the water in *f* (in presence of antimony, a solution of tartaric acid in dilute hydrochloric acid is substituted for the water in *f*); the flask *f* is connected with *h*, the connecting tube reaching down to the bottom of the fluid in the latter; the chlorine issuing from *h* is conducted into milk of lime, or into alcohol, or into the open air.

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* Pour a *perfectly cold* mixture of 45 parts of sulphuric acid and 21 of water, over one of 18 parts of powdered chloride of sodium and 15 of *finely powdered* binoxide of manganese, and shake, when a steady evolution of chlorine will at once begin, which, when it shows signs of slackening, may be promoted by a *gentle heat.*

When the apparatus is arranged, the sulphide to be examined is weighed in a narrow glass tube, sealed at one end, and subsequently cautiously transferred from this tube to the bulb *e*, in the manner illustrated by Fig. 74, to prevent any portion of the substance getting into the ends of the bulb-tube.

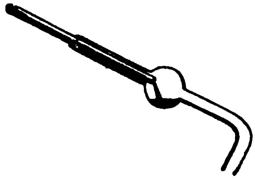

Fig. 74.

When the apparatus is filled with chlorine, *e* is connected with *d* by means of a vulcanized india-rubber tube, and the chlorine is allowed to act on the sulphide, at first without the aid of heat. When no further alteration is observed, a very gentle heat is applied to the bulb, care being taken also to keep the tube *g* warm, securing it thus from being stopped up by the sublimate of a volatile metallic chloride. The sulphide is completely decomposed by the chlorine, the metals being converted into chlorides, which partly remain in the bulb, partly—(viz. the volatile ones, as chloride of antimony, chloride of arsenic, chloride of mercury)—pass over into the receiver; the sulphur combines with the chlorine to chloride of sulphur, which passes over into the flask *f*, where, coming in contact with water, it decomposes with the latter, forming hydrochloric acid and hyposulphurous acid, with separation of sulphur. The hyposulphurous acid decomposes again into sulphur and sulphurous acid, which latter is finally, by the action of the chlorine water in *f*, converted into sulphuric acid. The final result of the decomposition is consequently sulphuric acid and a greater or less amount of separated sulphur. The operation is concluded when no more products of distillation—with the exception, perhaps, of sesquichloride of iron, the complete expulsion of which need not be awaited—pass over from the bulb. Heat is then applied to *e*, proceeding from the bulb towards the bend, so as to force all the chloride of sulphur which may remain in that part to pass over into *f*.

The apparatus is left undisturbed a short time longer, after which the tube *e* is cut off under the bend at *g*, and the separated end, which contains a portion of the volatile chlorides, closed by inverting over it a glass-tube sealed at one end and moistened inside. The whole is now allowed to stand 24 hours, to allow the volatile chlorides to absorb moisture, which will render them soluble in water without generating heat. The metallic chlorides in the cut-off end of the tube are then dissolved in dilute hydrochloric acid, the end is rinsed, and the solution added to the contents of the flasks *f* and *h*; a very gentle heat is now applied until the free chlorine is expelled, and the fluid is then allowed to stand until the sulphur has solidified. The sulphur is filtered off on a weighed filter, washed, dried, and weighed. The filtrate is precipitated with chloride of barium (§ 132), by which operation the amount of that portion of the sulphur is determined which has been converted into sulphuric acid. The fluid filtered off from the sulphate of baryta contains, besides the excess of chloride of barium added, also the volatile metallic chlorides; which latter are finally determined in it by the proper methods, which will be found in Section V.

The chloride remaining in the bulb-tube is either at once weighed as such (chloride of silver, chloride of lead), or where this is impracticable —as in the case of copper, for instance, which remains partly as subchloride partly as chloride—it is dissolved in water, hydrochloric acid, nitrohydrochloric acid, or some other suitable solvent, and the metal or metals in the solution are determined by the methods already described, or which will be found in Section V. To be enabled to ascertain the weight of the bulb-tube containing the chloride of silver or chloride of lead, it is advisable to reduce the chlorides by hydrogen gas, and then dissolve the metals in nitric acid.

2. *Methods in the Humid Way.*

a. Oxidation of the Sulphur by Acids yielding Oxygen.[*]

a. Weigh the finely pulverized sulphide in a small glass tube sealed at one end, and drop the tube into a tolerably capacious strong flask with glass stopper, which contains red fuming nitric acid (perfectly free from sulphuric acid) in more than sufficient quantity to effect the decomposition of the sulphide. Immediately after having dropt in the tube, close the flask. When the action, which is very impetuous at first, has somewhat abated, shake the flask a little; as soon as this operation ceases to cause renewed reaction, and the fumes in the flask have condensed, take out the stopper, rinse this with a little nitric acid, letting the rinsings run into the flask, and then heat the latter gently.

aa. The whole of the Sulphur has been oxidized, the Fluid is perfectly clear.[†]

Dilute with much water, and determine the sulphuric acid formed as directed in § 132. Do not neglect to wash the precipitate thoroughly with hot water, and to ascertain, after weighing, whether it is absolutely insoluble in dilute hydrochloric acid. Separate the bases in the filtrate from the excess of the salt of baryta by the proper methods, which will be found in Section V.

bb. Undissolved Sulphur floats in the Fluid.

Add chlorate of potassa in small portions, or strong hydrochloric acid, and digest some time on a water-bath. This process will often succeed in dissolving the whole of the sulphur. Should this not be the case, and the undissolved sulphur appear of a pure yellow color, dilute with water, collect on a weighed filter, wash carefully, dry, and weigh. After weighing, ignite the whole, or a portion of it, to ascertain whether it is perfectly pure. If a fixed residue remains (consisting commonly of quartz, gangue, &c., but possibly also of sulphate of oxide of lead, sulphate of baryta, &c.,) deduct its weight from that of the impure sulphur. In the filtered fluid, determine the sulphuric acid as in *aa*, calculate the sulphur in it, and add the amount to that of the undissolved sulphur. If the residue left upon the ignition of the undissolved sulphur contains an insoluble sulphate, decompose this as directed in § 132, and add the sulphur found in it to the principal amount.

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[*] In presence of lead, baryta, strontia, lime, tin, and antimony, method *b* is preferable to *a*.

[†] This can of course be the case only in absence of metals forming insoluble salts with sulphuric acid. If such metals are present, proceed as in *bb*, as it is in that case much more difficult to judge whether complete oxidation of the sulphur has been attained.

In the presence of bismuth, the addition of chlorate of potassa or of hydrochloric acid is not advisable, as chlorine interferes with the determination of bismuth.

β. Mix the finely pulverized metallic sulphide, in a dry flask, by shaking, with chlorate of potassa (free from sulphuric acid), and add concentrated hydrochloric acid in small portions. Cover the flask with a watch-glass, or with an inverted small flask. When the whole of the chlorate of potassa is decomposed, heat gently on the water-bath, until the fluid smells no longer of chlorine. Proceed now as directed in *a*, *aa*, or *bb*, according to whether the sulphur is completely dissolved or not. In the latter case you must of course immediately dilute and filter. The oxidation of the sulphur may be effected also by heating with nitric acid and chlorate of potassa.

γ. Strong nitrohydrochloric acid is also often used instead of the oxidizing agents named in α and β; however, with this the complete conversion of the sulphur into sulphuric acid succeeds more rarely.

b. Oxidation of the Sulphur by Chlorine in Alkaline Solution (*Rivot*, *Beudant*, and *Daguin's* Method,—suitable, also, for determining the sulphur in native brimstone. ("Compt. Rend.," 1853, 835.—"Journ. f. prakt. Chem.," 61, 134).

Heat the very finely pulverized sulphide or crude sulphur, for several hours with solution of potassa, free from sulphuric acid (which dissolves free sulphur, as well as the sulphides of arsenic and antimony), and then conduct chlorine into the fluid. This speedily oxidizes the sulphur; the sulphuric acid formed combines with the potassa to sulphate, which dissolves in the fluid, whilst the metals converted into oxides remain undissolved. Filter, acidify the alkaline filtrate, and precipitate the sulphuric acid from it by chloride of barium (§ 132). Arsenic and antimony pass into the alkaline solution in the form of sulphur acids, but not so lead, which is converted into binoxide, and remains completely undissolved. This method is, therefore, more particularly suited in presence of sulphide of lead. In presence of sulphide of iron, sulphate of potassa is formed at first, and hydrate of sesquioxide of iron, which, if the action of the chlorine is allowed to continue, will be converted into ferrate of potassa. As soon, therefore, as the fluid commences to acquire a red tint, the transmission of chlorine must be discontinued, and the fluid gently heated for a few moments with powdered quartz, to decompose the ferric acid formed.

It occasionally happens, more particularly in presence of quartz sand, iron pyrites, oxide of copper, &c., that the process is attended with impetuous disengagement of oxygen, which almost completely prevents the oxidizing action of the chlorine. However, this accident may be guarded against by reducing the substances to be analysed to the very finest powder.

c. Determination of the sulphur in dissolved sulphides of the alkalies and alkaline earths.[*]

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[*] Sulphides containing hyposulphite or sulphate are analysed as directed § 168.

α. If the salts contain no excess of sulphur, the best way is to proceed as directed § 148, 1, *b*, or *c*.

β. If they contain an excess of sulphur, method II., *b*, is the most suitable.

γ. In either case, the bases are estimated best in a separate portion, which is decomposed by evaporation with hydrochloric acid or sulphuric acid.

THIRD GROUP.

NITRIC ACID.—CHLORIC ACID.

§ 149.

1. NITRIC ACID.

I. *Determination.*

Free nitric acid in a solution containing no other acid is determined most simply in the volumetric way, by neutralizing with a dilute solution of soda of known strength (compare Special Part, Section "*Acidimetry*"). The following method also effects the same purpose: mix the solution with baryta water, until the reaction is just alkaline, evaporate slowly in the air, nearly to dryness, dilute the residue with water, filter, wash the carbonate of baryta formed by the action of the carbonic acid of the atmosphere upon the excess of the baryta water, add the washings to the filtrate, and determine in the latter the baryta as directed in § 101. Calculate for each equivalent of baryta found an equivalent of nitric acid. The correctness of the results depends entirely upon the accuracy of the execution of the analytical process. Avoid the use of a large excess of baryta water, and take care not to filter the evaporated fluid before its alkaline reaction has completely disappeared.

II. *Separation of nitric acid from the bases, and determination of the acid in nitrates.*

The determination of nitric acid in nitrates remains still a difficult problem, which has of late years much occupied the attention of chemists. Before entering upon the consideration of the question, I would lay it down as a general rule, that whatever method may be selected, it should always first be tried repeatedly upon weighed quantities of a pure nitrate, to acquire some familiarity with the details of the rather complicated processes required for the analysis of nitrates.

a. Methods based upon the decomposition of the Nitric acid by protochloride of iron.

α. *Pelouze* ("Journ. f. prakt. Chem.," 40, 324), was the first to turn the action of free nitric acid upon protochloride of iron to account for the determination of nitric acid. The formula of the decomposition is as follows:

$$6\,Fe\,Cl + K\,O, N\,O_5 + 4\,H\,Cl = 4\,H\,O + K\,Cl + 3\,Fe_2Cl_3 + N\,O_2.$$

In *Pelouze's* method a weighed quantity of protochloride of iron in excess is used, and the portion which remains unchanged determined by solution of permanganate of potassa. The process is conducted as follows: Dissolve 2 grammes of pianoforte wire in 80—100 c.c. of pure concentrated hydrochloric acid, in a flask holding about 150 c.c., which is closed by a cork with a glass tube fitted in it; promote the solution by application of a gentle heat. When the wire is dissolved, add 1·2 grm. of the nitrate of potassa or an equivalent quantity of another nitrate to be analysed, replace the cork, and heat rapidly to boiling. After 5 or 6 minutes, pour the fluid, which has now again cleared, into a larger-sized flask, dilute largely with water, and proceed as directed § 112, 2, *a*. Though this method gives occasionally satisfactory results, it can never be fully relied on, in which view all agree who have subjected the question to a critical examination (compare *Fr. Mohr*, "Lehrbuch der Titrirmethode," I., 216 ; *Abel* and *Bloxam*, "Quart. Journ. of Chem. Soc.," IX., p. 97). The results of numerous experiments made in my own laboratory lead to the same conclusion.

The following may be mentioned as causes of the defectiveness of the method:

a. Action of the air upon the nitric oxide gas present in the flask, together with aqueous vapor, which leads to the re-formation of nitric acid ; this may be held to be the principal cause of the inaccuracy of the method.

b. Incomplete expulsion of the nitric oxide from the fluid, which leads to the reduction of a larger amount of permanganate of potassa solution than corresponds to the protochloride of iron ; this is to be apprehended only in the case of dilute solutions.

c. Escape of nitric acid before it has acted upon the protochloride of iron ; this is to be apprehended in cases where the fluid, after addition of the nitrate, is boiled very rapidly, and the excess of protochloride of iron is comparatively small.

d. Occasionally also loss of iron, owing to want of proper care in boiling, and to be apprehended more especially if part of the protochloride of iron deposits on the sides of the vessels above the fluid, in the solid state.

I have succeeded in modifying *Pelouze's* process so as to avoid all these sources of error, and to obtain perfectly accurate and reliable results. My process is conducted as follows :—

Select a long-necked tubulated retort of about 200 c.c. capacity, and fix it in a slightly slanting position. Introduce into the body of the retort about 1·5 grm. of fine pianoforte wire, accurately weighed, and add about 30 or 40 c.c. of pure fuming hydrochloric acid. Conduct now through the tubulature, by means of a glass tube reaching only about 2 centimetres into the retort, hydrogen gas washed by transmission through solution of potassa, and connect the neck of the retort with a U-tube containing some water. Place the body of the retort on a water-bath, and heat gently until the iron is dissolved. Let the contents of the retort cool in the current of hydrogen gas ; increase the latter, and drop in, through the neck of the retort, into the body, a small tube containing a weighed portion of the nitrate under examination, which should not contain more than about 0·200 grm. of nitric acid. After restoring the connection between the neck and the U-tube, heat the contents of the retort in the water-bath for about a quarter of an hour, then remove the water-bath, heat with the lamp to boiling, until the fluid, to which the nitric oxide gas absorbed had imparted a dark tint, shows the color of sesquichloride of iron, and continue boiling for some minutes longer. Care must be taken to give the fluid an occasional shake, to prevent the deposition of dry salt on the inner side of the retort. Before you discontinue boiling, increase the current of hydrogen gas, that no air may enter through the U-tube when the lamp is removed. Let the contents cool in the current of hydrogen gas, dilute copiously with water free from air, and determine the iron still present as protochloride by permanganate of potassa solution

—168 of iron converted by the nitric acid from the state of proto- to that of sesquichloride correspond to 54 of nitric acid. Direct experiments, made with pure nitrate of potassa, gave 100·1 – 100·03 – 100·3, and 100·5, instead of 100 of nitric acid (see Experiments, No. 87).

β. *Schlösing's* method ("Annal. de Chim.," 3 sér. tom. 40, 479; "Journ. f. prakt. Chem.," 62, 142.

The following method, employed by *Schlösing*, more particularly to determine nitric acid in tobacco, and which affords this very important advantage, that it may be used also in presence of organic matters, has successfully passed through the ordeal of numerous and searching experiments.

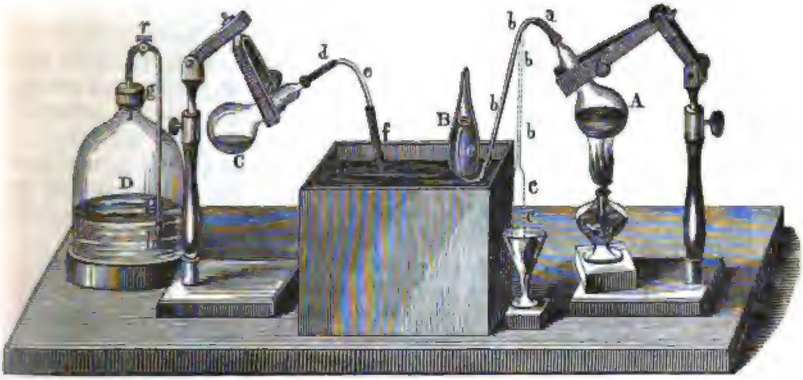

Fig. 75.

The process is conducted in the apparatus shown in Fig. 75.

The dissolved nitrate is introduced into the balloon A, whose neck is connected, by means of a vulcanized india-rubber tube *a*, with a narrow glass-tube *b*; *c* is another narrow caoutchouc-tube connected with *b*, and 15 centimetres long. The solution of the salt, which must be neutral or alkaline, is boiled down to a small volume, the aqueous vapor completely expelling the air from A and the tubes; *c* is dipped into a glass containing a solution of protochloride of iron in hydrochloric acid; the lamp removed, and the receding of the acid regulated by compressing the caoutchouc tube *c* with the fingers; when the iron solution is nearly absorbed, some hydrochloric acid is allowed to recede, three or four times, in separate portions, to free the tube completely from protochloride of iron, which is absolutely necessary. Before air can force its way, *c* is closed by an iron compression clamp, dipped under the mercury in the trough, with the end placed under the bell B. The lamp is now replaced under A, to allow the reaction to proceed; immediately after, the clamp is opened, and the tube simply compressed by the fingers, which are also removed from it as soon as a pressure is felt from within. The reaction is generally terminated in about eight minutes, when *c* is removed from under B. The latter is a small bell-jar, made in the form of an adapter; it must hold three or four times the volume of the gas to be received; in cases where the evolution of gas is rather impetuous, it is occasionally necessary to submerge the bell-jar in the trough, to effect a more speedy cooling of the vapor. The upper part of B is drawn out, as shown in Fig. 76, to facilitate the insertion of the neck *c* of the caoutchouc-tube, and also the breaking off the point. The bell-jar is first filled with water, to expel the air from it, then with mercury; milk of lime, previously boiled, is then finally introduced into it, by means of a curved pipette, which serves to free the nitric oxide gas entering B from every trace of acid vapor. The nitric oxide gas has now to be transferred to another balloon, C, to be there reconverted into nitric acid by oxygen. The balloon C contains some water; it is connected by a caoutchouc-tube, *d*, with a glass-tube, *e*, which bears at the opposite end another thin caoutchouc-tube, *f*, 10 centimetres in length.

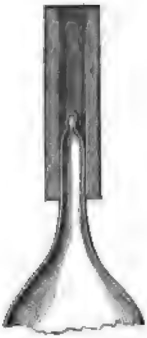

Fig. 76.

The water in C is now heated to boiling, until *all* air is expelled from the balloon and the tubes by the aqueous vapor; *f* is connected with the point of the bell-jar, B, which has just before been slightly cut with a diamond, and the end of the point then broken off. The aqueous vapor condenses at first in the bell-jar, which serves also to expel the small quantity of milk of lime remaining in the point. But if the lamp is now removed, a current in the opposite direction speedily sets in, which drives the nitric oxide gas into the balloon, C. Should this proceed too rapidly, *f* need simply be compressed with the fingers. As soon as the milk of lime in the bell-jar has nearly reached the rim of *c*, *f* is closed by a compression clamp. To transfer the last traces of the nitric oxide gas to C, pure hydrogen gas (20 or 30 c.c.) is conducted into the bell-jar, and allowed to be absorbed as before. *f* is then closed by the compression clamp, the end of the tube taken off from the point of the bell-jar, and connected instead with the glass-tube, *h*, of the oxygen-jar, D; the cork, *r*, is now opened, and then the compression clamp also, which will cause oxygen to pass from the jar into the balloon, C. When the object of the operation has been attained, *r* is closed, and *h* and *f* are disconnected; after waiting a quarter of an hour, the free nitric acid reproduced in C is determined by means of very dilute solution of soda (§ 215).

The success of this method depends essentially upon the complete expulsion of the air from A and C. *Schlösing* obtained highly satisfactory results by it. Where the quantity of nitric acid is only small, it is advisable to increase the amount of protochloride of iron considerably. For the determination of very minute quantities of nitric acid (under 0·010 grm., *Schlösing* employs a somewhat modified apparatus, for a description of which I refer to his paper on the subject, in the "Annal. de Chim.," 3 sér. tom. 40, 479.

γ. *Ville's* method ("Compt. rend.," 41, 939 and 987).

In this method, the nitric oxide gas evolved from the nitrate by protochloride of iron and hydrochloric acid is converted into ammonia, which is then received in a standard acid, as in § 99, 3. Small quantities of nitric oxide (obtained from 0·5 grm. or less of nitrate of potassa), are converted into ammonia by conducting the disengaged gas, mixed with an excess of hydrogen gas, over spongy platinum, heated nearly to redness; larger quantities, by conducting the gas, mixed with an excess of sulphuretted hydrogen, over soda-lime heated nearly to redness (NO_2 +

$3\,HS + 2\,CaO = NH_3 + CaO, SO_3 + CaS_2$). Fig. 77 shows the plan of the apparatus required. F is an apparatus for the evolution of hydrogen, E, the washing-bottle belonging to it; D serves for the reaction of the nitrate on the protochloride of iron; C is a sulphuretted hydrogen

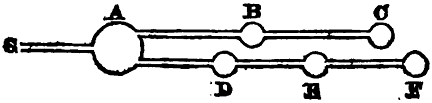

Fig. 77.

apparatus; B, the washing-bottle belonging to it. The glass tubes proceeding from B and D lead to the flask A, where they dip under mercury; a few pieces of chloride of calcium are placed in the mercury to retain the water which finds its way into A. The tube proceeding from A leads to another, which contains soda-lime, and is placed in a combustion-furnace; the free end of the latter tube is afterwards connected with a *Varrentrapp* and *Will's* absorption apparatus, which contains a measured quantity of acid of known strength (§ 187).

When the apparatus is prepared, solution of protochloride of iron in an excess of hydrochloric acid is introduced into D, to the amount of, at least, 100 grammes; if much organic matter is present, as in the case of molasses, for instance, it even requires as much as 300 or 400 grammes of a saturated solution of protochloride of iron, together with 3 or 4 grammes of concentrated hydrochloric acid. If there is much frothing of the organic matter, some butter should be added. The nitrate is now introduced into the flask D, and hydrogen transmitted through it for 10 minutes, to expel the air; after some time, the tube with the soda-lime is also heated, and, as soon as no more aqueous vapors are observed, connected with the absorption-apparatus, the transmission of hydrogen being continued, but at a slower rate. Sulphuretted hydrogen is now also evolved in C, and heat shortly after applied to D, so that by the time the contents begin to boil, about 3 or 4 centimetres of the soda-lime are decomposed. The evolution of sulphuretted hydrogen must now proceed briskly, the bubbles of gas following each other in rapid succession. After 10 minutes' boiling, the disengagement of sulphuretted hydrogen is discontinued, hydrogen being then still transmitted through the apparatus for 4 or 5 minutes. At least 15 centimetres of the soda-lime must remain undecomposed. When the operation is terminated, the contents of the nitrogen bulbs are determined as directed in § 99, 3.

Ville has tried this method on nitrate of potassa with very satisfactory results.

b. Method based upon the oxidation of Arsenious to Arsenic Acid.

Mix the compound with 3 times its weight of arsenious acid; dissolve the mixture in concentrated hydrochloric acid, evaporate to dryness, dissolve the residue in water, supersaturate the solution with ammonia, precipitate with a mixture of chloride of ammonium and sulphate of magnesia, and determine the precipitated arsenate of ammonia and magnesia as directed in § 127, 2, *a* (*J. Stein*). The results are accurate; comp. Analytical Notes and Experiments, No. 88.

c. Method based upon measuring the Nitric Oxide Gas expelled from the analysed Compound. *Walter Crum's* method ("Journ. f. prakt. Chem.," 41, 201).

Fill a graduated tube, made of strong glass, about 30 centimetres long and 2 centimetres wide, with mercury, and invert in the trough. Put a weighed sample of the substance under examination (about 0·1 grm.) into a very small tube, which must be nearly filled by it, and paste gummed paper over the open end of the tube. Now introduce this into the mercurial tube, and add, by means of a pipette with curved point, somewhat less than a cubic centimetre of water, and then about 3 c.c. of sulphuric acid, and let it stand for about 2 hours, with occasional shaking, but without application of heat. After this, note the difference of the mercury column, and the state of the barometer and thermometer, as well as the height of the sulphuric acid, then add about 20 c.c. of a warm solution of sulphate of protoxide of iron, and let it stand for 3 or 4 hours, with occasional stirring. Read off again as before. The absorbed gas is nitric oxide, of which the specific gravity is 1·0399, and 1000 c.c. consequently weigh, at 32° F., and 29·8 Bar., 1·3509 grm. *W. Crum* obtained satisfactory results by this convenient method.

d. Methods in which the Nitrogen of the Nitric Acid is separated and measured in the gaseous form.

These methods are more particularly suitable for analysing nitrates which are decomposed by ignition into oxide or metal and oxides of nitrogen; they will be found in the Section on the Ultimate Analysis of Organic Bodies, § 185. *Marignac* ("Annal. de Chim. et de Phys.," 27, 315) employed them to analyse compounds of nitric acid with suboxide of mercury. *Bromeis* ("Annal. d. Chem. u. Pharm.," 72, 38), analysed nitrite, &c., of oxide of lead by a similar method, recommended by *Bunsen*. In cases where it is intended to determine the water of the analysed nitrite in the direct way, it is almost indispensable to employ these methods.

e. Nitrates may often be analysed also by precipitating the base with carbonate of baryta, baryta water, or sulphide of barium, removing from the filtrate, if necessary, the excess of baryta by carbonic acid, heating, filtering, determining the dissolved baryta after § 101, and reckoning for each equivalent of it 1 equivalent of nitric acid; or by decomposing the nitrate, at boiling heat, with a solution of caustic or carbonate of soda of known strength, filtering, washing, and determining, by the alkalimetrical method, the remaining caustic or carbonate of soda (§ 220). The difference between the remaining quantity of soda and that originally present shows the amount of nitric acid contained in the analysed compound. Of course, the result can only be correct if no basic nitrate has precipitated along with the oxide or carbonate.

f. In anhydrous nitrates, the acid may often be determined from the loss of weight suffered upon fusion with 3 parts of fused borax (see § 139, II., *d*). *Schaffgotsch* obtained accurate results by this method ("Poggend., Annal.," 57, 260).

g. Gladstone ("Journ. f. prakt. Chem.," 64, 442) proposes to distil the nitric acid with sulphuric acid, and determine it with baryta as in I. This can give no reliable results, as hyponitric acid is apt to form in the process, which remains combined with the sulphuric acid or escapes, at least in part. *Martin's* method, lastly, ("Compt. rend.," 37, 947), which consists in decomposing the nitrate with an excess of zinc (NO_5 : Zn :: 1 : 5), water, and hydrochloric or sulphuric acid (to be added in small portions), and estimating the ammonia formed, gave me most unsatisfactory results. Even with application of much larger proportions of zinc, and after allowing the action to continue for several days, a considerable proportion of nitric acid was left undecomposed.

§ 150.

2. Chloric Acid.

I. *Determination.*

Free chloric acid in aqueous solution may be determined by converting it into hydrochloric acid by the agency of sulphuretted hydrogen, and determining the amount of the acid formed, as directed in § 169; or by saturating with solution of soda, evaporating the fluid, and treating the residue as directed in II., *a* or *b*.

II. *Separation of Chloric Acid from the Bases, and Determination of the Acid in Chlorates.*

a. Bunsen's method (" Ann. der Chem. und Pharm.," 86, 282).

When warm hydrochloric acid is made to act upon chlorates, the latter are reduced; as this reduction is not attended with separation of oxygen, the following decompositions may take place :—

$$\begin{matrix}\mathrm{Cl\,O_5}\\ \mathrm{H\,Cl}\end{matrix}\left\{\begin{matrix}\mathrm{Cl\,O}\\ \mathrm{Cl\,O_4}\\ \mathrm{H\,O}\end{matrix}\right.\quad \begin{matrix}\mathrm{Cl\,O_5}\\ \mathrm{2\,H\,Cl}\end{matrix}\left\{\begin{matrix}\mathrm{3\,Cl\,O}\\ \mathrm{2\,H\,O}\end{matrix}\right.\quad \begin{matrix}\mathrm{Cl\,O_5}\\ \mathrm{3\,H\,Cl}\end{matrix}\left\{\begin{matrix}\mathrm{2\,Cl\,O}\\ \mathrm{2\,Cl}\\ \mathrm{3\,H\,O}\end{matrix}\right.\quad \begin{matrix}\mathrm{Cl\,O_5}\\ \mathrm{4\,H\,Cl}\end{matrix}\left\{\begin{matrix}\mathrm{Cl\,O}\\ \mathrm{4\,Cl}\\ \mathrm{4\,HO}\end{matrix}\right.\quad \begin{matrix}\mathrm{Cl\,O_5}\\ \mathrm{5\,H\,Cl}\end{matrix}\left\{\begin{matrix}\mathrm{6\,Cl}\\ \mathrm{5\,H\,O}\end{matrix}\right.$$

Which of these products of decomposition may actually be formed, whether all or only certain of them, cannot be foreseen. But no matter which of them may be formed, they all of them agree in this, that, in contact with solution of iodide of potassium, they liberate for every equivalent of chloric acid in the chlorate, 6 equivalents of iodine. 761·28 of iodine liberated correspond accordingly to 75·46 of chloric acid. The analytical process is conducted exactly as described in the determination of chromic acid (compare § 130, *d*, *β*); or proceed according to the directions of § 142, *b*, if you wish to determine the disengaged chlorine by the latter method.

b. Proceed exactly as directed in § 142, 1, *c.* 12 equivalents of iron, converted from the state of proto- to that of perchloride, correspond to 1 equivalent of chloric acid.

c. The bases are appropriately determined, in a separate portion, by converting the chlorate into chloride, either by very cautious ignition, or by heating with hydrochloric acid.

For the determination of *hypochlorous acid*, I refer to the Special Part, article " *Chlorimetry.*"

SECTION V.

SEPARATION OF BODIES.

§ 151.

HAVING thus disposed of the methods which serve to determine the bases and acids in *simple* compounds, we will now proceed to discuss the various processes which are applied to effect the analysis of *complex* compounds or mixtures, and the determination of their several constituents, —in other words, to effect the separation of bodies from each other.

This end may be attained by two different ways, *a*, by *direct* analysis; and *b*, by *indirect* analysis.

By *direct* analysis, we understand the *actual* separation of the several individual acids or bases present in a compound or mixture. Thus, we separate potassa from soda by bichloride of platinum; copper from bismuth by cyanide of potassium; arsenic from iron by sulphuretted hydrogen; iodine from chlorine by nitrate of protoxide of palladium; phosphoric acid from sulphuric acid by baryta; carbon from nitrate of potassa by water, &c. &c. The principle of the methods of direct analysis, consequently, is to convert one of the two substances which it is intended to separate into an insoluble form, under circumstances which cause the solution of the other, or *vice versâ*. Or, occasionally, one of the two bodies may also be volatilized, whilst the other is left behind; or actual separation may be effected by some other means. This mode of analysis is preferable to the *indirect* way, and is therefore resorted to wherever the circumstances of the case will permit.

We term an analysis *indirect*, if it does not effect the *actual* separation of the substances which we wish to determine, but causes certain changes enabling us to infer or calculate the respective quantities of the individual bases or acids present in the analysed compound or mixture. Thus, for instance, the respective quantities of potassa and soda jointly present in a compound or mixture may be estimated by converting these two bases into sulphates, weighing the latter, and determining the proportion of sulphuric acid contained in them (§ 152, 3); thus, sesquioxide of iron may be estimated in presence of alumina, by weighing the mixed body, then determining the iron by volumetric analysis, and calculating the alumina from the difference, &c.

Indirect analysis, though applicable in an exceedingly great number of cases, is generally resorted to only to supply the deficiency of good methods of *actual* separation. It is impossible to point out every *special* case in which indirect analysis may be preferable to direct analysis; I have, therefore, confined myself to the indication of the more frequently occurring instances. For the calculations of indirect analyses, I refer to Subdivision B. (CALCULATION OF THE RESULTS). In certain cases, however, I have appended the mode of calculation to the description of the process.

For the sake of greater perspicuity and simplicity, I have retained our former subdivision into groups, and, as far as practicable, systematically arranged, first, the *general* separation of all the substances belonging to one group from those of the preceding group or groups; secondly, the separation of the several substances of one group from *all* or from certain substances of the preceding group or groups; and thirdly and finally, the separation of substances of one and the same group from each other. I think I need scarcely observe that the general methods which serve to separate the whole of the substances of one group from those of another group, are equally applicable to the separation of every individual substance of this group from one or several substances of the other group. I beg, moreover, to remark, that I do not intend to assert that the *special* methods given are preferable to the *general* methods, or that no other methods, besides those which I have selected for description in this work, might not be employed with equal or even better success in special cases. A wide field is left open here to the sagacity of the student.

In making a selection of certain general and special methods from the great number that have been proposed, I have been guided entirely by experience, and I have given the preference invariably to those which give the most accurate results. In cases where two equally accurate methods presented themselves, I have either given both, or selected the more simple of the two. I have, moreover, endeavored to point out, as far as possible, the particular circumstances under which either the one or the other of several methods deserves the preference. Methods which experience has shown to be defective or fallacious have been altogether omitted.

The methods given in this work are based in general upon the supposition that the base or acid to be separated exists in the free state, or in the form of a salt soluble in water. Where this is not the case, special mention is made of the circumstance.

Where the accuracy of an analytical method has been established already, in Section IV., no further allusion is made to the subject here. Paragraphs of former Sections deserving particular attention are referred to in parentheses.

The extension of chemical science introduces almost every day new analytical methods of every description, which are, justly or mistakenly, preferred to the older methods; the present time may therefore be looked upon in this, as in many other respects, as a period of transition, in which the new strives more than ever to overcome and supplant the old. I make this remark to show the impossibility of always adding to the description of a method an opinion of its usefulness and accuracy, and also to point out the importance, under such circumstances, of a proper systematic arrangement. To assist the student, I have in this Section arranged the various analytical methods upon the basis of their scientific principles, firmly persuaded that this will greatly tend to facilitate the study of the science, and will lead to endeavors to apply known and approved analytical methods to other bodies besides those to which they are already applied, or to discover new principles where experience has proved the old ones fallacious, and the methods based on them defective. To enable the student, on the other hand, to readily and promptly find all the methods adapted to effect the separation of bodies, I have, where necessary, placed at the head of the several paragraphs an index, which I think will answer the purpose of a guide in this respect. The *marginal numbers* are intended to serve the same purpose: the number in the index at the head of the several paragraphs, and also the numbers in the text, or without the § sign, refer to these.

I conclude these introductory remarks, with the important caution to the student, *never to look upon a separation as successfully accomplished, if he has not convinced himself, by the proper tests, that the separated substances are really free from every trace of the bodies from which it was intended to separate them.*

I. SEPARATION OF THE BASES FROM EACH OTHER.

FIRST GROUP.

POTASSA—SODA—AMMONIA ;—(*Lithia*).

§ 152.

Index : Potassa from soda, 1, 6 ;—from ammonia, 4, 5.
Soda from potassa, 1, 6 ;—from ammonia, 3, 4, 5.
Ammonia from potassa, 4, 5 ;—from soda, 3, 4, 5.
Lithia from the other alkalies, 7, 8, 9.

1. *Methods based upon the different Degrees of Solubility in Alcohol, of the Double Chlorides of the Alkali Metals with Bichloride of Platinum.*

a. POTASSA FROM SODA.

1 It is an indispensable condition in this method that the two alkalies should exist in the form of chlorides. If, therefore, they are present in any other form, they must be first converted into chlorides, which, in most cases, may be effected by evaporation with hydrochloric acid in excess ; but in presence of sulphuric acid, phosphoric acid, and boracic acid, this simple method will not answer. For the methods of separating the alkalies from the two latter acids, and converting them into chlorides, see §§ 135 and 136. The presence of sulphuric acid being a circumstance of rather frequent occurrence, the way of meeting this contingency is given below (2).

Determine the total quantity of the chloride of sodium and chloride of potassium,* dissolve in a small portion of water, add an excess of a concentrated neutral solution of bichloride of platinum in water, evaporate on the water-bath nearly to dryness, treat the residue with alcohol of from 76—80 per cent., cover the beaker or dish with a glass plate, and let the contents stand a few hours, with occasional stirring. If the fluid above the precipitate appears of a deep yellow color, this is a proof that a sufficient quantity of bichloride of platinum has been used ; if not, another portion of it must be added. When the sodio-bichloride of platinum has completely dissolved, and the potassio-bichloride of platinum at the bottom of the beaker or dish appears as a heavy yellow powder, with no crystalline scales of larger size discernible in it, filter the fluid from the precipitate, and treat the latter as directed in § 97. The quantity of the soda is usually estimated by subtracting from the united weight of the chloride of sodium and chloride of potassium the weight of the latter, calculated from that of the potassio-bichloride of platinum.

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* Never weigh the chlorides of the alkali metals before you have convinced yourself of their purity by dissolving them in water, which should give a clear solution, and testing this solution with ammonia and carbonate of ammonia, which must throw down no precipitate. It may be thought, perhaps, that a matter so simple need not be mentioned here ; still I have found that neglect in this respect is by no means uncommon.

To make quite sure that the potassa has completely separated, it is advisable to add to the filtrate some more bichloride of platinum, and, if the quantity of soda is only small, also some chloride of sodium; evaporate on the water-bath to dryness, at a temperature not exceeding ·167° F., and treat the residue in the manner just described. Should this operation again leave an undissolved residue of potassio-bichloride of platinum, let the separated particles quietly subside, decant the yellow fluid off from the trifling precipitate, wash the latter repeatedly with small quantities of spirit of wine by decantation, then transfer it to the filter which contains the principal precipitate, and wash, if necessary, again once or twice with small quantities of spirit of wine.

I prefer this way to ensure the complete separation of the potassa, to the usual process of evaporating the filtrate to dryness, igniting the residue with addition of some oxalic acid, or in a current of hydrogen, and determining the chloride of sodium in the solution obtained; since, after all, the estimation of the soda here is only *apparently* direct: if the chloride of potassium has not completely separated, the portion still remaining in the filtrate will, of course, be obtained now mixed with the chloride of sodium. The latter method can therefore only afford a control to determine whether a loss of substance has been sustained in the operation.

Should the solution contain sulphuric acid, it may be in presence of chlorine or of some volatile acid, convert the alkalies first into neutral sulphates (§§ 97 and 98), and weigh in that form. Dissolve in a little water, and add an alcoholic solution of chloride of strontium, slightly in excess. The quantity of spirit of wine in the fluid must be kept within limits which will not permit the separation of chloride of sodium or chloride of potassium. Allow to deposit, filter, and wash the sulphate of strontia (which may be weighed, by way of control—compare § 152, 3) with weak spirit of wine, until the washings no longer leave a residue upon evaporation on a watch-glass; evaporate the filtrate until the spirit of wine is completely driven off, dissolve the residue in a very small quantity of water, add bichloride of platinum, and proceed as directed above. The minute portion of chloride of strontium added in excess dissolves, either in that form, or as strontio-bichloride of platinum, together with the sodio-bichloride of platinum, in spirit of wine. 2

Instead of this method, which I commonly employ, the following processes may also be resorted to:—Dissolve the sulphates of the alkalies in water, and add baryta water, free from alkali, as long as a precipitate forms; let deposit, filter, wash the precipitate, and conduct carbonic acid into the filtrate, to throw down the excess of baryta; heat to boiling, filter the precipitated carbonate of baryta, wash, add hydrochloric acid to the filtrate, and evaporate to dryness. Or, add solution of bicarbonate of baryta in excess, then ammonia, and filter without applying heat.—Or, dissolve the weighed sulphated alkalies in water, add solution of acetate of baryta, free from chloride of barium, in the least possible excess; let deposit, filter, evaporate the filtrate to dryness, ignite the residue, treat with water, saturate cautiously with hydrochloric acid, and treat the solution of the chlorides of the alkali metals as directed above. Instead of acetate of baryta, you may also use acetate of lead, removing the excess of lead by sulphuretted hydrogen, and evaporating the filtrate with hydrochloric acid to dryness. Or, you may substitute chloride of lead for the acetate, heat to boiling, and omit the addition of hydrochloric acid in evaporating the filtrate (*L. Smith*).—Or, you may mix the sulphates with chloride of ammonium in powder, in a crucible, ignite, add a few drops of water and again some chloride of ammonium, ignite once more, and repeat this until the weight remains constant (*H. Rose*). This latter method I can recommend only where the chlorides contain a comparatively small admixture of sulphate; where this is the case, however, the process is very convenient, as there is no need in it of previously converting the whole mixture into sulphates.

Repeated experiments have shown that the process of separating potassa and soda, as described above, gives always a little less potassa than is really present. If the process is properly conducted, the loss of potassa amounts to about 1 per cent. I have found that it is usually greater in cases where the concentrated solution of the metallic chlorides is mixed with bichloride of platinum, and then with a rather large quantity of alcohol.

b. AMMONIA FROM SODA.

The process is conducted exactly as in *a*. See also § 99, 2. If potassa also is present, the precipitate produced by bichloride of platinum is ammonio-bichloride of platinum + potassio-bichloride of platinum; in which case the weighed precipitate is cautiously ignited until the chloride of ammonium is expelled (§ 124, *b*), the residue treated with water, and the chloride of potassium in the solution obtained determined as directed § 97, 3. The weight found is calculated upon potassio-bichloride of platinum, and the result deducted from the weight of the whole precipitate: the difference gives the weight of the ammonio-bichloride of platinum. The separated platinum may be weighed by way of control. 3

2. *Methods based upon the Volatility of Ammonia and its Salts.*
AMMONIA FROM SODA AND POTASSA.

a. The salts of the alkalies to be separated contain the same volatile acid, and admit of the total expulsion of their water by drying at 212° F., *without losing ammonia* (*e. g.* the metallic chlorides). 4

Weigh the total mass of the salts in a platinum crucible, and heat, with the lid on, gently at first, but ultimately for some time to faint redness; let the mass cool, and weigh. The decrease of weight gives the quantity of the ammonia salt. If the acid present is sulphuric acid, you must, in the first place, take care to heat very gradually, as otherwise you will suffer loss from the decrepitation of the sulphate of ammonia: and, in the second place, bear in mind that part of the sulphuric acid of the sulphate of ammonia remains with the sulphates of the fixed alkalies, and that you must accordingly convert them into neutral salts, by ignition in an atmosphere of carbonate of ammonia, before proceeding to determine their weight (compare §§ 97 and 98). Chloride of ammonium cannot be separated in this manner from sulphates of the fixed alkalies, as it converts them, upon ignition, partly or totally into chlorides.

b. Some one or other of the conditions given in a is not fulfilled.

If it is impracticable to alter the circumstances by simple means so as to make the method *a* applicable, the fixed alkalies and the ammonia must be estimated separately in different portions of the compound under examination. The portion in which it is intended to determine the soda and potassa is ignited until the ammonia is completely expelled. The fixed alkalies are converted, according to circumstances, into chlorides or sulphates, and treated as directed § 152, 1. The ammonia is estimated, in another portion, in the manner directed § 99, 3. 5

3. *Indirect Methods.*

Of course, a great many of these may be devised; but the following is the most generally employed. 6

POTASSA FROM SODA.

Both alkalies are converted into neutral sulphates, or into chlorides (§§ 97 and 98), and weighed in that form; the amount of sulphuric acid or chlorine in them is estimated (see § 132 for sulphuric acid, § 141 for chlorine); and the respective quantities of the soda and potassa are calculated from these data (see below "Calculation of Analyses," § 200).

The indirect method of determining potassa and soda is applicable only in the analysis of mixtures containing tolerably large quantities of both bases; but where this is the case, the process answers very well, affording also, more particularly, the advantage of expedition, if the chlorine in the weighed chlorides is determined volumetrically (§ 141, *b*).

Supplement to the First Group.

SEPARATION OF LITHIA FROM THE OTHER ALKALIES.

Lithia may be separated from *potassa* and *soda* in the indirect way, or by either of the following two methods:— 7

a. Treat the chlorides, dried at 248° F., with a mixture of equal volumes of absolute alcohol and anhydrous ether, digest for 24 hours, with occasional shaking, decant on to a filter, and treat the residue again several times with smaller portions of the mixture of alcohol and ether (*Rammelsberg*, "Pogg. Annal.," 66, 79). Determine, on the one part, the undissolved chloride of potassium and sodium; on the other, the dissolved chloride of lithium, by distilling the fluid off, and converting the chloride of lithium into sulphate. This method is apt to give too much lithium, as chloride of sodium and chloride of potassium are not absolutely insoluble in a mixture of alcohol and ether. The results may be rendered more accurate by treating the impure chloride of lithium, obtained by distilling off the ethereo-alcoholic fluid, once more with the mixture of alcohol and ether, with addition of a drop of hydrochloric acid, adding the residue left to the principal residue, and then only converting the chloride of lithium into sulphate. If the chlorides, which it is intended to treat with alcohol and ether, have been ignited, however so gently, caustic lithia is formed by the action of water, and carbonate of lithia by attraction of carbonic acid; in that case it is necessary, therefore, to add a few drops of hydrochloric acid, in the process of digestion.

b. Weigh the mixed alkalies, best in form of sulphates, and then determine the lithia or phosphate of lithia according to the directions of § 100. If the quantity of lithia is relatively very small, convert the weighed sulphates into chlorides (2), separate, in the first place, the potassa and soda by means of alcohol, and then determine the lithia (*Mayer*, "Annal. d. Chem. u. Pharm.," 98, 193). As regards the application of this method, I have to observe that, whilst *Mayer* asserts that the compound $3\,Li\,O, P\,O_5$ is actually formed under the circumstances stated in § 100, *Rammelsberg* ("Pogg. Annal.," 102, 443) still maintains the correctness of his former statement, viz., that the new compound has, indeed, the formula $3\,R\,O, P\,O_5$, but contains NaO and Li O in varying proportions; and, in fact, consists perhaps of a combination of $3\,Li\,O, P\,O_5 + 3\,Na\,O, P\,O_5$, mixed with variable proportions of $3\,Li\,O, P\,O_5$. 8

From *potassa* alone lithia may be separated in the same way as soda, by means of bichloride of platinum. The separation of lithia from *ammonia* may be effected like that of soda from ammonia. 9

SECOND GROUP.

BARYTA—STRONTIA—LIME—MAGNESIA.

I. SEPARATION OF THE OXIDES OF THE SECOND GROUP FROM THOSE OF THE FIRST.

§ 153.

Index: Baryta from potassa and soda, 10, 12;—from ammonia, 11.
Strontia from potassa and soda, 10, 13;—from ammonia, 11.
Lime from potassa and soda, 10, 14;—from ammonia, 11.
Magnesia from potassa and soda, 15, 24;—from ammonia, 11.

A. *General Method.*

1. THE WHOLE OF THE ALKALINE EARTHS FROM POTASSA AND SODA. 10

Principle on which the method is based: Carbonate of ammonia precipitates, from a solution containing chloride of ammonium, only baryta, strontia, and lime.

Mix the solution, in which the bases are assumed to be contained in the form of chlorides, with a sufficient quantity of chloride of ammonium to prevent the precipitation of the magnesia by ammonia; add some ammonia, then carbonate of ammonia in slight excess, let the mixture stand covered for 12 hours in a moderately warm place, filter, and wash the precipitate with water to which a few drops of ammonia have been added.

The *precipitate*, which contains the *baryta*, *strontia*, and *lime*, is treated as directed in § 154; the *filtrate* contains the *magnesia* and the *alkalies*, and, besides these, exceedingly minute traces of lime, and somewhat more considerable traces of baryta, as the carbonates of these two earths are not absolutely insoluble in a fluid containing chloride of ammonium. In ordinary analyses these minute admixtures may be disregarded; but in cases where a higher degree of accuracy is required, they must be removed. To accomplish this, add to the filtrate 3 or 4 drops (but not much more) of dilute sulphuric acid, then a few drops of oxalate of ammonia, and let the fluid stand again for 12 hours in a warm place. If a precipitate forms, collect this on a small filter, wash, and treat on the filter with some dilute hydrochloric acid, which dissolves the oxalate of lime, and leaves the sulphate of baryta undissolved.

Evaporate the filtrate, which contains the *magnesia* and the *alkalies*, according to circumstances, either at once, or after previous removal of the traces of lime and baryta, to dryness, and remove the ammonia salts by gentle ignition in a covered crucible, or in a small covered dish of platinum or porcelain.* In the residue, separate the magnesia from the alkalies by one of the methods given in § 153, B, 4 (15—24).

2. THE WHOLE OF THE ALKALINE EARTHS FROM AMMONIA.—The same principle and the same process as in the separation of potassa and soda from ammonia (see § 152). 11

B. *Special Methods.*

SINGLE ALKALINE EARTHS FROM POTASSA AND SODA.

1. BARYTA FROM POTASSA AND SODA.

12 Precipitate the baryta with dilute sulphuric acid (§ 101, 1, *a*), evaporate the filtrate to dryness, and ignite the residue, with addition of carbonate of ammonia (§ 97, 1—98, 1). Take care to add a sufficient quantity of sulphuric acid to convert the alkalies also completely into sulphates.

This method is, on account of its greater accuracy, preferable to the one in A, in cases where the baryta has to be separated only from one of the two fixed alkalies; but if both alkalies are present, the other method is more convenient, since the alkalies are obtained in it as chlorides.

2. STRONTIA FROM POTASSA AND SODA.

13 Strontia may be separated from the alkalies, like baryta, by means of sulphuric acid; but this method (precipitation of the strontia as sulphate) is not preferable to the one in A (10), in cases where the choice is permitted (compare § 102).

3. LIME FROM POTASSA AND SODA.

14 Precipitate the lime with oxalate of ammonia (§ 103, 2, *b*, *a*), filter, evaporate the filtrate to dryness, and determine the alkalies in the ignited residue. In determining the alkalies, dissolve the residue, freed by ignition from the ammonia salts, in water, and filter the solution from the undissolved portion; acidify the filtrate, according to circumstances, with hydrochloric acid or sulphuric acid, and then evaporate to dryness; since oxalate of ammonia partially decomposes chlorides of the alkali metals upon ignition, and converts the bases into carbonates, except in presence of a large proportion of chloride of ammonium. The results are still more accurate than in A, ex-

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* This operation effects also the removal of the small quantity of sulphuric acid added to precipitate the traces of baryta, as sulphates of the alkalies are converted into chlorides of the alkali metals upon ignition in presence of a large proportion of chloride of ammonium.

cept where oxalate of ammonia has been used, after the precipitation by carbonate of ammonia, to remove the minute traces of lime from the filtrate.

4. Magnesia from Potassa and Soda.

a. Methods based upon the sparing solubility of Magnesia in Water.

α. Make a solution of the bases, as neutral as possible, and free from ammonia salts (whether the acid is sulphuric acid, hydrochloric acid, or nitric acid, is indifferent), add baryta-water as long as a precipitate forms, heat to boiling, filter the fluid off from the precipitate, and wash the latter with boiling water. The precipitate contains the magnesia as hydrate; the magnesia is determined either as directed in § 104, 1, *b*, or the precipitate is dissolved in hydrochloric acid, the baryta thrown down with sulphuric acid, and the magnesia as phosphate of magnesia and ammonia (104, 2). The alkalies, which are contained in the solution, according to circumstances, as chlorides, nitrates, or caustic alkalies, are separated from the baryta as directed in **10** or **12**. *Liebig*, who was the first to employ this method, proposes crystallized sulphide of barium as precipitant. The method gives good results, but is rather tedious. **15**

β. Precipitate the solution with a little pure milk of lime, boil, filter, and wash. Separate the lime and the magnesia in the precipitate as directed § 154; the lime and the alkalies in the filtrate, as directed in **10** or **14**. This method is advantageously employed in cases where it is desirable to remove the magnesia from a fluid containing lime and alkalies, which latter alone it is intended to determine. **16**

γ. Evaporate the solution of the chlorides (which must contain no other acids) to dryness, and, if chloride of ammonium is present, ignite; warm the residue with a little water; this will dissolve it with the exception of some magnesia, which separates. Add to the solution elutriated oxide of mercury, evaporate to dryness on the water-bath, with frequent stirring, and proceed exactly as directed § 104, 3, *b*. There is no need to continue the ignition until the whole of the oxide of mercury is expelled; on the contrary, part of it may be filtered off together with the magnesia, and subsequently volatilized upon the ignition of the latter. The solution contains the alkalies in form of chlorides (*Berzelius*). This method gives satisfactory results. Take care to add the oxide of mercury only in proper quantity, and always test the solution of the alkaline chlorides for magnesia, of which it will generally be found to retain a trace. **17**

δ. Add to the solution of the chlorides oxalic acid in sufficient quantity to convert all the bases present, viewed as potassa, into quadroxalate; add some water, evaporate to dryness, in a platinum dish, and ignite. **18**

By this operation the chlorides of the alkali metals are partially, the chloride of magnesium completely, converted into oxalates, which, upon ignition, give carbonated alkalies and magnesia. The salts of the alkalies are separated from the magnesia by boiling water. If the solution looks a little turbid, evaporate to dryness, treat the residue with water, and filter off the trifling amount of magnesia still remaining; add, finally, hydrochloric acid to the filtrate, and determine the alkalies as chlorides.

If the bases are present in form of sulphates, add to the boiling solution chloride of barium, until the formation of a precipitate just ceases, evaporate the filtrate with an excess of oxalic acid, and proceed as in **18**. Separate the undissolved carbonate of baryta, which remains mixed with the magnesia, from the latter as directed § 154. 19

We owe these methods to *Mitscherlich;* they have recently been described by *Lasch* ("Journ. f. prakt. Chem.," 63, 343). I can add my own testimony to the accuracy of the results.

I cannot recommend *Sonnenschein's* method (boiling the chlorides with carbonate of oxide of silver), as the filtrate invariably retains more than mere traces of magnesia.

The method described in **18**, may also be successfully employed with nitrates, for which it is, indeed, specially recommended by *Deville* ("Journ. f. prakt. Chem.," 60, 17). Carbonic acid and nitrous acid gas are evolved in the process of evaporation. 20

b. Method based upon the Precipitation of Magnesia by Phosphate of Ammonia or Arsenate of Ammonia.

Add to the solution containing magnesia, potassa, and soda, ammonia in excess, and some chloride of ammonium, should this not be present already; precipitate the magnesia with a slight excess of pure phosphate of ammonia. Filter, remove the free ammonia from the filtrate by evaporation, and then precipitate the phosphoric acid with acetate of lead as a combination of phosphate of lead and chloride of lead. Remove the excess of oxide of lead from the still hot fluid by ammonia and carbonate of ammonia, filter, and determine the potassa and soda in the filtrate as directed §§ 97 and 98. (*O. L. Erdmann*, "Journ. f. prakt. Chem.," 41, 89; *Heintz*, "Pogg. Annal.," 73, 119). I cannot concede the preference to this method over those given in *a*. The following process is much more simple: precipitate the magnesia with arsenate of ammonia, instead of phosphate, and estimate it as arsenate of magnesia as directed § 127, 2. Evaporate the filtrate to dryness, and heat the residue in a porcelain crucible. Should the mass not have contained sufficient chloride of ammonium, add some of the latter substance to the residue, and then ignite again. As this operation effects the ready and complete volatilization of the arsenic acid, the alkalies are left behind as pure chlorides. I need hardly mention that proper arrangements to secure the safe removal of the arsenical fumes are indispensable. *C. v. Hauer* ("Jahrbuch d. K. K. geolog. Reichsanst.," Jahrgang IV., 863) recommends a similar method. 21 22

c. Indirect Method, which gives also, at the same time, the quantity of Potassa and Soda, if both are present.

Convert, with proper care, the bases into pure neutral sulphates, weigh, dissolve in water, and determine the sulphuric acid by chloride of barium (§ 132); filter, precipitate the excess of baryta from the filtrate by sulphuric acid, filter again, concentrate the filtrate by evaporation, and determine the magnesia as directed § 104, 2 (*K. List*, "Annal. d. Chem. u. Pharm.," 81, 117). 23

Calculate the magnesia found as sulphate, and deduct the resulting weight from the total weight of the sulphates: the difference shows the quantity of the sulphated alkalies; deduct also the sulphuric 24 acid combined with the magnesia from the total quantity of sulphuric acid: the difference gives the amount of sulphuric acid combined with the alkalies. See § 152, 3 (6).

II. SEPARATION OF THE OXIDES OF THE SECOND GROUP FROM EACH OTHER.

§ 154.

Index: Baryta from strontia, 26, 29;—from lime, 26, 28, 29;—from magnesia, 25, 27.
Strontia from baryta, 26, 29;—from lime, 32, 33;—from magnesia, 25.
Lime from baryta, 26, 28, 29;—from strontia, 32, 33;—from magnesia, 25, 30, 31.
Magnesia from baryta, 25, 27;—from strontia, 25;—from lime, 25, 30, 31.

A. *General Method.*

THE WHOLE OF THE ALKALINE EARTHS FROM EACH OTHER.

Proceed as in **10**. The magnesia is precipitated from the filtrate with phosphate of soda. The precipitated carbonates of the baryta, strontia, and lime, are dissolved in hydrochloric acid, and the bases separated as directed in **26**. **25**

B. *Special Methods.*

1. *Method based upon the Insolubility of Silicofluoride of Barium.*

BARYTA FROM STRONTIA AND FROM LIME.

Mix the neutral or slightly acid solution with hydrofluosilicic acid in excess, add a volume of spirit of wine equal or somewhat inferior to that of the fluid (*H. Rose*), let the mixture stand 12 hours, filter the precipitate of *silicofluoride of barium* on a weighed filter, wash with a mixture of equal parts of water and spirit of wine, until the washings cease to show even the least trace of acid reaction (but no longer), and dry at 212° F. Precipitate the strontia or lime from the filtrate by dilute sulphuric acid (§ 102, 1 *a*, and § 103, 1). The results are satisfactory. For the properties of silicofluoride of barium, see § 71. If both strontia and lime are present, the sulphates are weighed, converted into carbonates (§ 132, II., *b*), and the two bases then separated as directed in **32** or **33**. **26**

2. *Methods based upon the Insolubility of Sulphate of Baryta.*

a. BARYTA FROM MAGNESIA.

Precipitate the baryta with sulphuric acid (§ 101, 1, *a.*), and the magnesia from the filtrate with phosphate of soda and ammonia (§ 104, 2). **27**

b. BARYTA FROM LIME.

Mix the solution with hydrochloric acid, then with highly dilute sulphuric acid (1 part acid to 300 water), as long as a precipitate forms; let deposit, and determine the sulphate of baryta as directed in § 101, 1, *a*. Add to the filtrate the washings, concentrated pre- **28** viously by evaporation, neutralize the acid with ammonia, and precipitate the lime as oxalate (§ 103, 2, *b*, *a*). The results are accurate.

3. *Method based upon the different deportment with Carbonated Alkalies of Sulphate of Baryta on the one, and Sulphates of Strontia and Lime on the other hand.*

BARYTA FROM STRONTIA AND LIME.

Digest the precipitated sulphates of the three bases for 12 hours, at the common temperature, with frequent stirring, with a solution of carbonate of ammonia, decant the fluid on to a filter, treat the undissolved residue repeatedly in the same way, wash finally with water, and separate the undecomposed sulphate of baryta by means of dilute hydrochloric acid from the carbonate of strontia and lime formed (*H. Rose*, "Pogg. Annal.," XCV. 286, 299, 427). 29

4. *Methods based upon the Insolubility of Oxalate of Lime in Chloride of Ammonium and in Acetic Acid.*

LIME FROM MAGNESIA.

a. Mix the properly diluted solution with sufficient chloride of ammonium to prevent the formation of a precipitate by ammonia, which is added in very slight excess; add oxalate of ammonia as long as a precipitate forms, then a further portion of the same re-agent, about sufficient to convert the magnesia also into oxalate (which remains in solution). This excess is absolutely indispensable to ensure complete precipitation of the lime, as oxalate of lime is slightly soluble in solution of chloride of magnesium not mixed with oxalate of ammonia (Analytical Notes and Experiments, No. 89). Let the mixture stand 12 hours in a moderately warm place, remove the supernatant clear fluid, as far as practicable, from the precipitated oxalate of lime, mixed with a little oxalate of magnesia, by decanting on to filter, wash the precipitate once more in the same way by decantation, then dissolve in hydrochloric acid, add ammonia in slight excess, and oxalate of ammonia. Let the fluid stand until the precipitate has completely subsided, then pour on to a filter, transfer the precipitate finally to the latter, and proceed exactly as directed § 103, 2, *b*, *a*. The first filtrate contains the larger portion of the magnesia, the second the remainder. Evaporate the second filtrate, acidified with hydrochloric acid, to a small volume, then mix the two fluids, and precipitate the magnesia with phosphate of soda as directed in § 104, 2. If the quantity of ammonia salts present is considerable, the estimation of the magnesia is rendered more accurate by evaporating the fluids, in a large platinum or silver dish,* to dryness and igniting the residuary saline mass, divided in several portions, in a smaller platinum dish, until the ammonia salts are expelled. The residue is then treated with hydrochloric acid and water, heat applied, the fluid filtered† and the filtrate finally precipitated with ammonia and phosphate of soda. 30

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* A porcelain dish does not answer so well (see Analytical Notes and Experiments, No. 3).

† If the process of evaporation has been conducted in a silver vessel, a little chloride of silver will often separate.

Numerous experiments recently made in my laboratory have convinced me that this method, which is so frequently employed, gives accurate results only if the foregoing instructions are strictly complied with. It is only in cases where the quantity of magnesia present is relatively small, that one single precipitation with oxalate of ammonia may be found sufficient (comp. Anal. Notes and Experim., No. 90).

b. In the case of lime and magnesia combined with phosphoric acid, dissolve in the least possible quantity of hydrochloric acid, add ammonia until a copious precipitate forms; redissolve this by addition of acetic acid, and precipitate from the solution the lime with an excess of oxalate of ammonia. As free acetic acid by no means prevents the precipitation of small quantities of oxalate of magnesia, the precipitate contains some magnesia, and, as oxalate of lime is not quite insoluble in acetic acid, the filtrate contains some lime, which two sources of error compensate each other in some measure. In accurate analyses, however, these trifling admixtures of magnesia and lime are afterwards separated from the weighed precipitates of carbonate of lime and pyrophosphate of magnesia. 31

5. *Method based upon the Insolubility of Nitrate of Strontia in Alcohol.*

STRONTIA FROM LIME.

Treat the nitrates with absolute alcohol. Filter the fluid from the undissolved nitrate of strontia, wash with alcohol, dissolve in water, and determine as sulphate of strontia (§ 102, 1). Precipitate the lime from the filtrate by sulphuric acid. The results are approximate. This method is applicable only where the proportion of lime is large, that of strontia small. 32

6. *Indirect Method.*

STRONTIA AND LIME.

Determine both bases first as carbonates, precipitating them either with carbonate or with oxalate of ammonia (§ 102 and § 103); then estimate the amount of carbonic acid in them by fusion with fused borax (§ 139, II., *d*), and from the results calculate the amount of strontia and lime as directed in § 200. This method gives very accurate results, except either of the two bases be present in very small proportion only. 33

THIRD GROUP.

ALUMINA—SESQUIOXIDE OF CHROMIUM.

I. SEPARATION OF THE OXIDES OF THE THIRD GROUP FROM THE ALKALIES.

§ 155.

1. FROM AMMONIA.

a. Salts of alumina and of sesquioxide of chromium may be separated from salts of ammonia by ignition. However, in the case of alumina, this method is applicable only in the absence of chlorine (volatilization of chloride of aluminium). The safest way, therefore, is to mix the compound first with carbonate of soda, and ignite after. 34

b. Determine the ammonia by one of the methods given in § 99, 3, 35 using solution of potassa or soda to effect the expulsion of the ammonia. The alumina and sesquioxide of chromium are then determined in the residue in the same way as in 36.

2. FROM POTASSA AND SODA.

a. Precipitate and determine the sesquioxide of chromium and alumina as directed in § 105, *a*, and § 106, *a*. The filtrate contains the alkalies, which are then freed from the salt of ammonia formed, by evaporation to dryness and ignition. 36

b. *Alumina* may be separated also from potassa and soda, by heating the nitrates of the three bases (see 39). 37

II. SEPARATION OF THE OXIDES OF THE THIRD GROUP FROM THE ALKALINE EARTHS.

§ 156.

Index: 1. *Alumina* from baryta 38, 39, 40, 41, 42, 43;—from strontia 38, 39, 40, 41, 42, 43;—from lime, 38, 39, 40, 41, 42, 44, 45, 46;—from magnesia, 38, 39, 40, 41, 42, 45, 46.

2. *Sesquioxide of Chromium* from the alkaline earths, 47, 48.

1. SEPARATION OF ALUMINA FROM THE ALKALINE EARTHS.

A. *General Methods.*

THE WHOLE OF THE ALKALINE EARTHS FROM ALUMINA.

1. *Method based upon the Precipitation of Alumina by Ammonia, and upon its Solubility in Solution of Soda.*

Mix the hot solution, in a beaker, with chloride of ammonium, add a slight excess of ammonia, free from carbonic acid, place the beaker on a flat stoneware plate filled with ammoniated water, and invert over it a larger beaker, with the rim dipping into the ammoniacal fluid, by which means the carbonic acid of the atmosphere is effectively excluded. After 12 hours, decant, and then wash the hydrate of alumina exactly as directed § 105, *a*. The solution contains the baryta, strontia, and lime, with the greater part of the magnesia, the remainder of the latter being with the hydrate of alumina in a kind of chemical combination. The precipitate often contains, notwithstanding every precaution used to avoid it, also minute quantities of carbonate of baryta, strontia, and lime. Dissolve the hydrate of alumina in hydrochloric acid, by transferring it with a spatula, as far as practicable, to a platinum or porcelain dish, treating the filter with warm hydrochloric acid, to extract the last adhering particles of the hydrate, and employing the hydrochloric acid running off, to effect the solution of the precipitate in the dish; concentrate the fluid by evaporation, add pure solution of soda or potassa or, better still, pure solid hydrate of potassa or soda, until the precipitate of hydrate of alumina formed is redissolved; heat, filter off hot from the hydrate of magnesia which separates, wash the latter carefully with hot water, dissolve in some hydrochloric acid, mix with ammonia in excess, and add the clear solution to the filtrate of the first operation, which contains the larger portion of the magnesia; if the solution is not perfectly clear, filter off from the trifling 38 deposit of alumina, and add the filtrate to that of the first operation. It will be seen that in this way the minute quantities of carbonate of baryta, strontia, and lime, which have precipitated with the hydrate of alumina, are restored to the bulk of the substances in that filtrate. The further separation of the alkaline earths is effected by evaporating the fluid, acidified with hydrochloric acid, in a platinum dish, or in a glass flask, and adding to the concentrated warm fluid ammonia in slight excess. This usually produces a trifling precipitate of alumina, which is filtered off, washed, and weighed together with the principal precipitate. The alkaline earths are determined in the filtrate as directed § 154. The alumina is precipitated from the alkaline solution by strongly acidifying with hydrochloric acid, boiling with some chlorate of potassa (to destroy the traces of organic matter which the solution of soda or potassa may have dissolved out of the filter paper, and which would interfere with the precipitation of the alumina), and then adding ammonia (§ 105, *a*). If all that is required is to separate alumina from baryta, strontia, or lime, and the amount of the latter bodies is relatively large, it is often the best way to redissolve the tolerably well-washed alumina precipitate in hydrochloric acid, heat the solution for a considerable time, and then precipitate again with ammonia. By this course of proceeding the alumina is obtained perfectly free from alkaline earths.

2. *Method based upon the unequal Decomposability of the Nitrates at a Moderate Heat* (*Deville*, "Journ. f. prakt. Chem.," 1853, 60, 9).

To make this simple and convenient method applicable, the bases must be present as pure nitrates. Evaporate to dryness in a covered platinum dish, and heat gradually in the sand or air-bath—(or, better still, on a cylindrical iron plate similar to that described in § 31—see Fig. 36—with two cavities, one for the platinum dish, the other, filled with brass filings, for the thermometer)—to about 392°—482° F., until a glass rod moistened with ammonia ceases to indicate further evolution of nitric acid fumes. You may also, without risk, continue to heat until nitrous acid vapors form. The residue consists of alumina, nitrates of baryta, strontia, and lime, nitrate and basic nitrate of magnesia. 39

Moisten the mass with a concentrated solution of nitrate of ammonia, and heat gently, but do not evaporate to dryness. Repeat this operation until no further evolution of ammonia is perceptible. (The basic nitrate of magnesia, insoluble in water, dissolves in nitrate of ammonia, with evolution of ammonia, as neutral nitrate of magnesia.) Add water, and digest at a gentle heat.

If the nitrate of ammonia has liberated only imperceptible traces of ammonia, pour hot water into the dish, stir, and add a drop of dilute ammonia; this must cause no turbidity in the fluid; should the fluid become turbid, this proves that the heating of the nitrates has not been continued long enough; in which case you must again evaporate the contents of the dish, and heat once more.

The alumina remains undissolved in the form of a dense granular substance. Decant after digestion, and wash with boiling water; ignite strongly in the same vessel in which the separation has been effected, and weigh. Separate the alkaline earths as directed § 154. In the same way alumina may be separated also from potassa and soda.

3. *Method in which the processes of* 1 *and* 2 *are combined.*

Precipitate the alumina as in **38**, wash in the same way as there directed, then treat with nitric acid, and proceed according to the directions of **39**, to remove the trifling amount of magnesia, &c., which has fallen down with the alumina; add the solution obtained to the principal solution of the alkaline earths, and treat the fluid as directed in **38**. This excellent method may be employed also in the case of chlorides. **40**

4. *Method based upon the Precipitation of Alumina by Acetate of Soda upon boiling.*

The same process as in **57**, *d.* The results are satisfactory. **41**

5. *Method based upon the Formation of a Soluble Alkaline Aluminate in the dry way.*

See **100** (§ 161). **42**

B. *Special Methods.*

SOME OF THE ALKALINE EARTHS FROM ALUMINA.

1. *Method based upon the Precipitation of some of the Salts of the Alkaline Earths.*

a. BARYTA AND STRONTIA FROM ALUMINA.

Precipitate the baryta and strontia with *sulphuric acid* (§§ 101 and 102), and the alumina from the filtrate as directed § 105, *a.* This method is especially suited for the separation of baryta from alumina. **43**

b. LIME FROM ALUMINA.

Add ammonia to the solution until a permanent precipitate forms, then acetic acid until this precipitate is redissolved, then acetate of ammonia, and finally *oxalate of ammonia* in slight excess (§ 103, 2, *b*, *β*); allow the precipitated oxalate of lime to deposit in the cold, then filter, and precipitate the alumina from the filtrate as directed § 105, *a.* Compare also 99. **44**

2. *Methods based upon the Precipitation of Alumina by Bicarbonate of Soda or Carbonate of Baryta.*

a. ALUMINA FROM MAGNESIA, AND FROM SMALL QUANTITIES OF LIME.

Add to the rather dilute, moderately acid solution, in a flask or covered beaker, a cold prepared solution of bicarbonate of potassa or soda, as long as effervescence ensues and a precipitate forms; allow the fluid to stand 12 hours, then decant, filter 3 times, and wash with water containing carbonic acid.* The precipitate is hydrate of alumina containing an admixture of alkali; the whole of the magnesia is in the solution. Dissolve in hydrochloric acid, and throw down the alumina with ammonia, after addition of chloride of ammonium, in the manner directed § 105, *a.* Precipitate the magnesia **45** from the solution as basic phosphate of magnesia and ammonia (§ 104, 2).

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* This may be readily prepared by adding to a highly dilute solution of bicarbonate of potassa or soda, a small quantity of hydrochloric acid, insufficient to saturate the base.

This method, which was formerly much employed, may be resorted to also to effect the joint separation of both lime and magnesia from alumina; but satisfactory results can only be expected if the quantity of lime is very small. In cases of the kind, the fluid must be largely diluted before the bicarbonate of soda is added, and the precipitation must be effected in a stoppered flask. The precipitate of alumina is apt to retain some lime and magnesia.

b. ALUMINA FROM MAGNESIA, AND SMALL QUANTITIES OF LIME.

Mix the slightly acid dilute fluid, in a stoppered flask, with elutriated carbonate of baryta, in moderate excess; let the mixture stand in the cold until the hydrated alumina has completely subsided, wash by decantation three times, and then determine the alumina in the precipitate as directed **43**; the magnesia and lime in the filtrate as directed in § 154, after previous removal of the baryta by sulphuric acid, according to the directions of **28**. 46

2. SEPARATION OF SESQUIOXIDE OF CHROMIUM FROM THE ALKALINE EARTHS.

The best way to effect the separation of sesquioxide of chromium from all the alkaline earths at the same time, is to convert the sesquioxide into chromic acid. For this purpose the pulverized substance is mixed with 2½ parts of pure *carbonate of soda* and 2½ parts of *nitrate of potassa,* and the mixture heated in a platinum crucible to fusion. On treating the fused mass with hot water, the chromium dissolves as alkaline chromate; the residue contains the alkaline earths as carbonates, or in the caustic state (magnesia). The chromium in the solution is determined as directed § 130. 47

I need hardly observe that sesquioxide of chromium may also be separated from *baryta* and, though less perfectly, from *strontia,* by means of *sulphuric acid* added to the acid solution of the substance. Sesquioxide of chromium cannot be separated by ammonia from the alkaline earths, since, even though carbonic acid be completely excluded, particles of the alkaline earths are thrown down with the sesquioxide of chromium. From solutions containing a salt of sesquioxide of chromium, lime cannot be precipitated completely by oxalate of ammonia; but it may be by sulphuric acid and alcohol (§ 103, 1). 48

III. SEPARATION OF SESQUIOXIDE OF CHROMIUM FROM ALUMINA.

§ 157.

Fuse the oxide with two parts by weight of nitrate of potassa and 4 parts of carbonate of soda, in a platinum crucible, treat the fused mass with boiling water, rinse the contents of the crucible into a porcelain dish or beaker, add a somewhat large quantity of chlorate of potassa, supersaturate slightly with hydrochloric acid, evaporate to the consistence of syrup, and add, during the latter process, some more chlorate of potassa in portions, to remove the free hydrochloric acid. Dilute now with water, and precipitate the alumina by ammonia or carbonate of ammonia as directed in § 105, *a.* The alumina falls down free from sesquioxide of chromium. The chromium in 49 the filtrate is determined as directed § 130. If you omit the evaporation with hydrochloric acid and chlorate of potassa, part of the chromic will be reduced by the nitrous acid in the fluid, and sesquioxide of chromium will accordingly, upon addition of ammonia, precipitate with alumina (*Dexter*, "Pogg. Annal.," 89, 142).

FOURTH GROUP.

OXIDE OF ZINC—PROTOXIDE OF MANGANESE—PROTOXIDE OF NICKEL—PROTOXIDE OF COBALT—PROTOXIDE OF IRON—SESQUIOXIDE OF IRON.

I. Separation of the Oxides of the Fourth Group from the Alkalies.

§ 158.

A. *General Methods.*

1. All the Oxides of the Fourth Group from Ammonia.

Proceed as for the separation of sesquioxide of chromium and alumina from ammonia (34, § 155). It must be borne in mind that the oxides of the fourth group comport themselves, upon ignition with chloride of ammonium, as follows:—Sesquioxide of iron is partly volatilized as sesquichloride; the oxides of manganese are converted into protochloride of manganese, containing protosesquioxide of that metal; the oxides of nickel and cobalt are reduced to the metallic state; oxide of zinc volatilizes, with access of air, as chloride of zinc (*H. Rose*). It is, therefore, generally the safest way to add carbonate of soda. The ammonia is determined in a separate portion. 50

2. All Oxides of the Fourth Group from Potassa and Soda.

Mix with ammonia until the fluid is neutral, add *sulphide of ammonium*, and filter off the sulphides from the fluid containing the alkalies. The precautionary measures recommended in the case of sulphide of nickel (§ 110, *b*), must be carefully attended to, otherwise part of that sulphide will remain in solution. Acidify the filtrate with hydrochloric acid, concentrate by evaporation, filter from the sulphur, evaporate the filtrate to dryness, ignite the residue, to effect the removal of the ammonia salts, and determine the alkalies by the methods given in § 152. Nickel and cobalt may be separated from the alkalies also by the method given § 170, B, 2, *b* (67). 51

B. *Special Methods.*

1. Oxide of Zinc from Potassa and Soda, by precipitating the zinc from the solution of the acetate with sulphuretted hydrogen (see 66). 52
2. Protoxide of Nickel and Protoxide of Cobalt from the Alkalies, by igniting the chlorides in a stream of hydrogen gas (see 72).
3. Sesquioxide of Iron from Potassa and Soda, by precipitating the sesquioxide of iron with ammonia; or by heating the nitrates (see 39).
4. Protoxide of Manganese from the Alkalies.

a. Saturate the solution with *chlorine*, and precipitate the 53 manganese—as hydrated sesquioxide—with carbonate of baryta or ammonia. The latter precipitant is apt to leave some manganese in solution.

b. Precipitate the manganese with peroxide of lead (*Gibbs*); (see **58**). The acid with which the bases are combined may be hydrochloric acid, nitric acid, or sulphuric acid. If the choice is allowed, select the first.

c. Heat the nitrates (*Deville*); (see **58** γ).

II. SEPARATION OF THE OXIDES OF THE FOURTH GROUP FROM THE ALKALINE EARTHS.

§ 159.

Index: Oxide of zinc from baryta and strontia, 54, 55, 56, 60;—from lime, 54, 56, 60;—from magnesia, 54, 56.

Protoxide of manganese from baryta and strontia, 54, 55, 58, 59;—from lime and magnesia, 54, 58, 59.

Protoxides of nickel and cobalt from baryta and strontia, 54, 55, 60, 61;—from lime, 54, 60, 61;—from magnesia, 54, 61.

Sesquioxide of iron from baryta and strontia, 54, 55, 57;—from lime and magnesia, 54, 57.

A. *General Method.*

ALL OXIDES OF THE FOURTH GROUP FROM THE ALKALINE EARTHS. **54**

Add to the solution, in a flask with stopper, chloride of ammonium and, if acid, also ammonia, and precipitate with sulphide of ammonium, as in **51**. Take care to use slightly yellow sulphide of ammonium, perfectly saturated with sulphuretted hydrogen, and free from carbonate and sulphate of ammonia, and to employ it in sufficient excess. Insert the stopper, and let the flask stand for some time, to allow the precipitate to subside, then wash quickly, and as far as practicable, out of the contact of air, with water to which some sulphide of ammonium has been added. Acidify the filtrate with hydrochloric acid, heat, filter from the sulphur, and separate the alkaline earths, as directed in § 154.

If the quantity of the alkaline earths is rather considerable, it is advisable to treat the precipitate once more with hydrochloric acid, heat the solution gently for some time, and then re-precipitate in the same way. In presence of nickel and cobalt, it is not necessary to effect complete solution. These two latter metals may be separated also from the alkaline earths by the method given § 170, B, 2, *b* (**67**).

B. *Special Methods.*

1. BARYTA AND STRONTIA FROM THE WHOLE OF THE OXIDES OF THE FOURTH GROUP.

Precipitate the baryta and strontia from the acid solution with sulphuric acid (§§ 101 and 102). This method is preferable to any other to effect the separation of baryta from the oxides of the fourth group. **55**

2. OXIDE OF ZINC FROM THE ALKALINE EARTHS.

Convert the bases into acetates, and precipitate the zinc from the solution as directed in § 108, *b*. **56**

3. SESQUIOXIDE OF IRON FROM THE ALKALINE EARTHS.

a. Precipitate the dilute solution with bicarbonate of soda or with carbonate of baryta (see 45, 46). 57

b. Precipitate the sesquioxide of iron with succinate of ammonia (§ 113, 1, *c*).

c. Decompose the nitrates by heat (39).

d. Add carbonate of soda to the moderately dilute solution, until the fluid is nearly neutral and has acquired a deep brownish-red tint; add *acetate of soda*, boil for some time, wash three times by boiling, and then filter off the brownish-red precipitate, which contains all the sesquioxide of iron in form of a basic salt. Wash with boiling water to which some acetate of ammonia has been added. The thoroughly washed sequioxide of iron may either be dried, ignited, and weighed; or dissolved, whilst still moist, in hydrochloric acid, and the solution precipitated with ammonia (§ 113, 1 *c*). If you wish to avoid the use of fixed alkalies, you may substitute carbonate and acetate of ammonia for the corresponding soda salts. The results are satisfactory.

e. Precipitate with *ammonia*, conducting the operation exactly as directed 38. If you wish to employ this method in presence of rather large quantities of iron and magnesia, you must re-dissolve in hydrochloric acid the hydrated sesquioxide of iron containing magnesia, and precipitate with bicarbonate of soda. With small quantities of iron, it is generally sufficient to re-dissolve the precipitate in hydrochloric acid, and precipitate again with ammonia.

4. PROTOXIDE OF MANGANESE FROM THE ALKALINE EARTHS.

a. Methods based upon the separation of Manganese as Sesquioxide or Binoxide.

a. Gibbs's Method ("Annal. der Chem. und Pharm.," 86, 54).—Add to the *perfectly* neutral solution of the bases, which may be combined with hydrochloric acid or nitric acid,* or, in the case of magnesia, with sulphuric acid, pure binoxide of lead,† in the proportion of 5 grammes of the binoxide to 1 gramme of substance; digest for an hour at about 185° F., with frequent stirring, filter the fluid from the precipitate, which contains the whole of the manganese, probably as sesquioxide, and wash with boiling water. If magnesia is present, let the digested fluid cool, then add a few drops of nitric acid before proceeding to filtration. Determine the alkaline earths (and alkalies) in the filtrate as directed in §§ 152 and 154. Ignite the precipitate, dissolve in strong nitric acid, and separate the manganese and lead as directed in § 162. This method is a little complicated. Presence of free hydrochloric acid does not interfere with the process, but free nitric acid and sulphuric must not be present; compare *Will*, "Annal. der Chem. und Pharm.," 86, 62. 58

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* Hydrochloric acid deserves the preference if, besides the alkaline earths, alkalies are present; if not, nitric acid is preferable.

† The binoxide of lead prepared from minium is not adapted for use in this process, on account of the impurities which it contains. Pure binoxide may be obtained by treating the hydrated oxide diffused in water, with chlorine, washing the product with boiling water, digesting with nitric acid, and washing.

β. *Schiel's* Method (*Sillim.* Journal, 15, 275).—Add to the hydrochloric acid solution carbonate of soda until the fluid is nearly neutralized, mix with acetate of soda, and then conduct *chlorine gas* into the mixture. The acetate of protoxide of manganese is decomposed, and the whole of the manganese separates as binoxide. The alkaline earths remain in solution. Experiments made by *Rivot*, *Beudant* and *Daguin*, and also in my laboratory, have shown that an acetic or nitric acid solution answers better than one in hydrochloric acid. The acetic or nitric acid solution is kept heated to between 122° and 140° F., whilst the chlorine gas is transmitted through it; as soon as the binoxide has separated, the transmission of the gas is stopped. In an experiment made by me, I found that the protosesquioxide of manganese obtained by the ignition of the binoxide so produced contained alkali. The binoxide must therefore be dissolved in hydrochloric acid, and the solution precipitated as directed § 109, 1, *a*. Instead of chlorine gas, solution of hypochlorous acid or of hypochlorite of soda may be used. In using the latter, care must be taken to keep the fluid always slightly acid by acetic acid. The method is good.

γ. *Deville's* Method ("Journ. f. prakt. Chem.," 60, 11).—The bases must be present as nitrates. Heat in a covered platinum dish to from 392° to 482° F., until the formation of fumes has completely ceased, and the mass has become black; and proceed in all other respects as directed in **39**. The presence of a small quantity of organic matter, or the action of a too intense heat, may cause the reduction of traces of binoxide of manganese, and their solution in nitrate of ammonia; these traces will be found with the magnesia.

δ. Saturate the solution with chlorine gas, or, if the quantity of manganese is very minute, with chlorine water, and precipitate the manganese as hydrated oxide, with bicarbonate of soda or carbonate of baryta (*H. Rose*). Before weighing the protosesquioxide of manganese, you must make quite sure that it contains no admixture of alkali (see β).

b. Methods based upon the Volumetric Determination of Manganese, according to *Bunsen* and *Krieger* ("Annal. der Chem. und Pharm.," 87, 268).

a. MANGANESE FROM MAGNESIA.

Precipitate with solution of soda (§ 109, 1, *b*). Wash the precipitate thoroughly, ignite, and weigh. If the quantity of magnesia present is sufficient, the residue has the formula, 59

$$Mn_2O_3, MgO + x MgO.$$

Treat a weighed sample of it as directed in § 142, towards the end; this will give the quantity of the manganese (1 equivalent of chlorine, or of liberated iodine, corresponds to 1 equivalent of Mn_2O_3); from the difference you may calculate the quantity of the magnesia.

β. FROM BARYTA AND STRONTIA.

Precipitate with carbonate of soda (§ 109, 1, *a*). The ignited precipitate has the formula,

$$Mn_2O_3, BaO + x BaO, CO_2.$$

Treat a sample as in *a*; this will give the quantity of the manganese. To find that of the carbonate of baryta, deduct the weight of the sesquioxide of manganese from that of the weighed precipitate, and add to the difference so much carbonic acid as has been expelled by the sesquioxide of manganese, that is, for each equivalent of $Mn_2 O_3$, an equivalent of $C O_2$.

γ. FROM LIME.

Proceed as in β; but after ignition, moisten the residue with carbonate of ammonia, evaporate again to dryness, and ignite gently, and repeat the same operation until the weight remains constant.

In the case of lime it is better to ignite the precipitate over the blast gas-lamp until the lime is reduced to the caustic state.

N.B. This method of volumetric determination of manganese presupposes the presence of more than 1 equivalent of $Mg O$, $Ca O$, &c., to 1 equivalent of $Mn_2 O_3$; for if the case is different, the residue contains, besides $Mn_2 O_3$, also $Mn_3 O_4$, $Mn O$. To adapt the method also to cases of the latter description, *Krieger* recommends the following process: dissolve a sample of the weighed precipitate, add half the weight of oxide of zinc, precipitate with carbonate of soda, ignite the precipitate some time in the air, determine the quantity of the residue, and use the latter or an aliquot part of it, for the volumetric determination. This residue contains the whole of the manganese as Mn_2O_3.

5. PROTOXIDE OF COBALT, PROTOXIDE OF NICKEL, AND OXIDE OF ZINC, FROM BARYTA, STRONTIA, AND LIME.

Mix with carbonate of soda in excess, add cyanide of potassium, heat very gently, until the precipitated carbonates of protoxide of cobalt, protoxide of nickel, and oxide of zinc are redissolved; then filter the cyanide of potassium solution of the metallic cyanides off from the carbonated alkaline earths. Dissolve the latter in dilute hydrochloric acid, and separate them as directed in § 154. Separate the metals as directed § 160. 60

6. PROTOXIDE OF COBALT AND PROTOXIDE OF NICKEL FROM MAGNESIA.

Precipitate with a mixture of solution of hypochlorite of potassa and solution of caustic potassa. The precipitate consists of peroxide of nickel, sesquioxide of cobalt, and hydrate of magnesia; wash thoroughly, and digest, whilst still moist, at a temperature of from 86° to 104° F., with an excess of solution of chloride of mercury. In this process, a double salt is formed of $Mg Cl + 3 Hg Cl$, and the magnesia is dissolved, whilst a corresponding quantity of basic chloride of mercury precipitates (*Ullgren*, *Berzel.*, "Jahresber.," 21, 146). Evaporate the solution and washings, with addition of pure oxide of mercury, and determine the magnesia as directed § 104, 3, *b*. Remove the mercury from the oxides of nickel and cobalt by ignition, and separate the two metals as directed below. 61

7. PROTOXIDE OF COBALT AND PROTOXIDE OF NICKEL FROM BARYTA, STRONTIA, AND LIME.

Ignite the chlorides of the metals in hydrogen gas (72).

III. SEPARATION OF THE OXIDES OF THE FOURTH GROUP FROM THOSE OF THE THIRD, AND FROM EACH OTHER.

§ 160.

Index: Alumina from oxide of zinc, 62, 63, 66, 80, 83;—from protoxide of manganese, 62, 63, 64, 74, 75, 80, 92;—from protoxide of nickel, 62, 63, 65, 83;—from protoxide of cobalt, 62, 63, 65, 83;—from protoxide of iron, 62, 63, 64, 65;—from sesquioxide of iron, 63, 64, 65, 69, 90.

Sesquioxide of chromium from oxide of zinc, protoxide of manganese, protoxide of nickel, protoxide of cobalt, and protoxide of iron, 62, 63, 73;—from sesquioxide of iron, 63, 69, 73.

Oxide of zinc from alumina, 62, 63, 66, 80, 83;—from sesquioxide of chromium, 62, 73;—from protoxide of manganese, 66, 74, 75, 93;—from protoxide of nickel, 66, 68, 71, 87, 88;—from protoxide of cobalt, 66, 68, 71, 85, 88;—from sesquioxide of iron, 62, 66, 77, 80, 89, 91.

Protoxide of manganese from alumina, 62, 63, 64, 74, 75, 80, 92;—from sesquioxide of chromium, 62, 63, 73;—from oxide of zinc, 66, 74, 75, 93;—from protoxide of nickel, 67, 68, 72, 74, 75, 76;—from protoxide of cobalt, 67, 68, 72, 86;—from sesquioxide of iron, 62, 77, 78, 80, 92.

Protoxide of nickel from alumina, 62, 63, 65, 83;—from sesquioxide of chromium, 62, 63, 73;—from oxide of zinc, 66, 68, 71, 82, 87, 88;—from protoxide of manganese, 67, 68, 72, 74, 75, 76, 82;—from protoxide of cobalt, 76, 82, 84;—from sesquioxide of iron, 62, 67, 77, 78, 91.

Protoxide of cobalt from alumina, 62, 63, 65, 83;—from sesquioxide of chromium, 62, 63, 73;—from oxide of zinc, 66, 68, 71, 82, 85, 88;—from protoxide of manganese, 67, 68, 72, 82, 86;—from protoxide of nickel, 76, 82, 84;—from sesquioxide of iron, 62, 67, 77, 81.

Protoxide of iron from alumina, 62, 63, 64, 65—from sesquioxide of chromium, 62, 63, 73;—from sesquioxide of iron, 62, 70, 79, 91, 94.

Sesquioxide of iron from alumina, 63, 64, 65, 69, 90;—from sesquioxide of chromium, 63, 69, 73;—from oxide of zinc, 62, 66, 77, 80, 89, 91;—from protoxide of manganese, 62, 77, 78, 80, 92;—from protoxide of nickel, 62, 67, 77, 78, 91;—from protoxide of cobalt, 62, 67, 77, 81;—from protoxide of iron, 62, 70, 79, 91, 94.

A. *General Methods.*

1. *Method based upon the Precipitation of some Oxides by Carbonate of Baryta.*

SESQUIOXIDE OF IRON, ALUMINA, AND SESQUIOXIDE OF CHROMIUM, FROM ALL OTHER OXIDES OF THE FOURTH GROUP.

Mix the sufficiently dilute solution, which must contain a little free acid,* in a flask, with a moderate excess of elutriated carbonate of 62 baryta diffused in water; insert the stopper and let the mixture stand some time in the cold, with occasional shaking. The sesquioxide of iron, alumina, and sesquioxide of chromium, are completely separated,* whilst the other bases remain in solution, with the exception perhaps of traces of protoxide of cobalt and protoxide of nickel, which will generally fall down with the precipitated oxides. This may be prevented, at least as regards nickel, by addition of chloride of ammonium to the fluid to be precipitated (*Schwarzenberg*, "Annal. d. Chem. u. Pharm.," 97, 216). Decant, stir the solid particles up with cold water, let deposit, decant again, filter, and wash with cold water. The precipitate contains, besides the precipitated oxides, carbonate of baryta; and the filtrate, besides the non-precipitated oxides, a salt of baryta.

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* If there is much free acid, the greater part of it must first be saturated with carbonate of soda.

If protoxide of iron is present, and it is wished to separate it by this method from sesquioxide of iron, &c., the air must be excluded during the whole of the operation. In that case, the solution of the substance, the precipitation, and the washing by decantation, are effected in a flask (see Fig. 78, A), through which carbonic acid is transmitted (*d*). The washing water, boiled free from air, and cooled out of contact of air, is poured in through a funnel tube (*c*), and the fluid drawn off by means of a moveable siphon (*b*); both *b* and *c* are fitted air-tight into the cork; they are smeared with tallow.

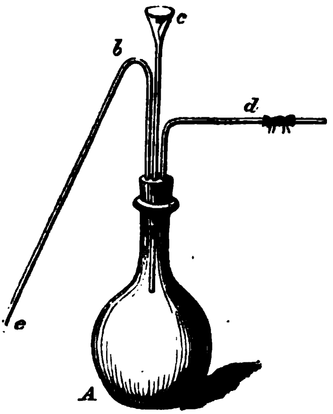

Fig. 78.

2. *Method based upon the Precipitation of the Oxides of the Fourth Group, by Sulphide of Sodium, from Alkaline Solution effected with the aid of Tartaric Acid.*

ALUMINA AND SESQUIOXIDE OF CHROMIUM FROM THE OXIDES OF THE FOURTH GROUP.

Mix the solution with tartaric acid, then with pure solution of 63
soda or potassa until the fluid has cleared again;† add sulphide of sodium as long as a precipitate forms, allow it to deposit until the supernatant fluid no longer exhibits a greenish or brownish tint; decant, stir the precipitate up with water containing sulphide of sodium, decant again, transfer the precipitate, which contains all the metals of the fourth group, to a filter, wash with water containing sulphide of sodium, and separate the metals as directed in B. Add to the filtrate nitrate of potassa, and evaporate to dryness; fuse the residue, and separate the alumina from the chromic acid formed, as directed § 157.

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* The separation of the sesquioxide of chromium requires the most time.

† Sesquioxide of chromium and oxide of zinc cannot be obtained together in alkaline solution (*Chancel*, "Compt. rend.," 43, 927; "Journ. f. prakt. Chem.," 70, 378).

B. *Special Methods.*

1. *Methods based upon the Solubility of Alumina in Caustic Alkalies.*[*]

a. ALUMINA FROM PROTOXIDE AND SESQUIOXIDE OF IRON, AND SMALL QUANTITIES OF PROTOXIDE OF MANGANESE (but not from the protoxides of nickel and cobalt).

Heat the rather concentrated acid solution in a flask to boiling, 64 remove from the fire, and reduce the sesquioxide of iron present by sulphite of soda. Replace the fluid on the fire, keep boiling some time, and then neutralize with carbonate of soda, add solution of pure soda or potassa in excess, and boil for some time.

If the analysed substance contains much iron, the precipitate will become black and granular, which is a proof that the iron has been converted into protosesquioxide. The tendency to bumping, preceding the actual ebullition of the fluid, may be guarded against by means of a spiral coil of platinum wire placed in the liquid, or by constant agitation of the latter; when ebullition has once set in, there is no further need of these precautions. Remove the fluid now from the fire, allow to deposit, pass the clear fluid through a filter, which must not be over-porous, boil the precipitate again with a fresh quantity of solution of soda, then wash it, first by decantation, afterwards on the filter with hot water. Acidify the alkaline filtrate with hydrochloric acid, boil with some chlorate of potassa (38), concentrate by evaporation, and precipitate the alumina as directed § 105, *a* ("Journ f. prakt. Chem.," 45, 261). The boiling of the precipitated oxides with the solution of soda is effected best in a somewhat capacious silver or platinum dish. A solution of soda containing alumina and silica must be particularly avoided.

If sesquioxide of chromium was present in the analysed substance, you will find the principal portion of this with the sesquioxide of iron; but a small quantity has been oxidized in the process and converted into chromic acid, and is accordingly found in the fluid filtered from the alumina.

b. The method described in *a* is often employed also in a modified form, omitting the reduction of the sesquioxide of iron; in which case the process is performed as follows:—Precipitate with ammonia, decant, filter, wash, transfer the precipitate still moist to a platinum dish, without the aid of water, and remove the last particles adhering to the filter by means of warm hydrochloric acid. The washings of the filter are kept separate. When the precipitate in the platinum dish has dissolved, add, very cautiously, concentrated solution of carbonate of soda, until the free acid is almost neutralized, then apply heat, finally to boiling; after this, remove the lamp, and add a lump of pure hydrate of potassa. sufficiently large to redissolve the precipitated alumina, leaving the hydrated sesquioxide of iron undissolved. Rinse the platinum dish now into the beaker which contains the washings of the filter; wash the sesquioxide of iron, first by decantation, then upon the filter with boiling water, and treat the filtrate as in *a*.

If the fluid from which it is intended to separate sesquioxide of iron and alumina, contains lime or magnesia, some alumina is likely to remain undissolved.

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[*] Instead of solution of potassa or soda, ethylamine may also be used to effect the separation of alumina from iron (*Sonnenschein*, "Journ. f. prakt. Chem.," 67, 148).

c. ALUMINA FROM SESQUI- AND PROTOXIDE OF IRON, PROTOXIDE OF COBALT, AND PROTOXIDE OF NICKEL.

Fuse the oxides with hydrate of potassa in a silver crucible, boil the mass with water, and filter the alkaline fluid, which contains the alumina, from the oxides, which are free from alumina, but contain potassa (*H. Rose*). 65

2. *Methods based upon the different deportment of the several Sulphides with Acids, or of the Acetic Acid Solutions with Sulphuretted Hydrogen.*

a. OXIDE OF ZINC FROM ALUMINA AND THE OXIDES OF THE FOURTH GROUP.

The solution of the acetates, which must be free from inorganic acids, and must contain a sufficient excess of acetic acid, is precipitated with sulphuretted hydrogen, which throws down the zinc only (§ 108, *b*). The oxides are usually most readily obtained, in acetic acid solution, by converting them into sulphates, and adding a sufficient quantity of acetate of baryta. Sulphuretted hydrogen is then conducted, without application of heat, into the unfiltered fluid, to which, if necessary, some more acetic acid has been added. Should the precipitate, as will sometimes happen, look gray, this may be remedied, if the coloration proceeds from admixture of sulphide of iron in the precipitate, by applying a gentle heat, and once more conducting sulphuretted hydrogen into the fluid. The precipitate, which consists of a mixture of sulphide of zinc and sulphate of baryta, is washed with water containing sulphuretted hydrogen. It is then heated with hydrochloric acid, the solution filtered, and the zinc in the filtrate determined as directed § 108, *a*. The other oxides in the fluid filtered off from the sulphide of zinc are, after previous removal of the baryta by precipitation, determined by the proper methods. 66

b. PROTOXIDE OF COBALT AND PROTOXIDE OF NICKEL FROM PROTOXIDE OF MANGANESE AND THE OXIDES OF IRON.

The solution of the oxides, which must be free from nitric acid, is, after previous neutralization of any free acid which may be present by ammonia, precipitated with sulphide of ammonium, and highly dilute hydrochloric acid (*H. Rose*), or acetic acid (*Wackenroder*) then added, and sulphuretted hydrogen gas conducted into the fluid to saturation, with frequent stirring. This serves to dissolve the sulphide of manganese and the sulphide of iron, whilst the sulphide of cobalt and the sulphide of nickel, though the latter less completely, remain undissolved. The sulphides of the metals are reprecipitated from the filtrate by addition of ammonia and sulphide of ammonium, and the precipitate is treated once more with dilute hydrochloric acid, &c. The results are nearly accurate. It is advisable, however, to test the weighed cobalt and nickel compounds, for manganese and iron. 67

c. PROTOXIDE OF COBALT AND PROTOXIDE OF NICKEL FROM PROTOXIDE OF MANGANESE AND OXIDE OF ZINC.

α. Put the weighed mixture of the oxides in a small porcelain or platinum boat, insert this into a tube, heat to dull redness, whilst conducting sulphuretted hydrogen gas over it. Let the sulphides of 68 the metals formed cool in the current of gas, and then digest them for several hours with cold dilute hydrochloric acid, which dissolves only the sulphide of manganese, and the sulphide of zinc. The sulphides of nickel and cobalt are left behind free from admixture of the other sulphides (*Ebelmen*).[*]

β. Precipitate with carbonate of soda, filter, wash, and ignite; mix 1 part of the residue with 1·5 of sulphur and 0·75 of carbonate of soda, and heat the mixture in a small retort as strongly as possible for half an hour. Allow the mixture to cool, and treat the sulphide of zinc (and sulphide of manganese) formed, with dilute hydrochloric acid (1 part of acid to 10 of water), *Brunner*.[†]

3. *Methods based upon the different deportment of the several Oxides with Hydrogen Gas at a red heat.*

a. Sesquioxide of Iron from Alumina and Sesquioxide of Chromium.

α. *Rivot's* Method. ("Ann. de Chim. et de Phys.," xxx 188; 69
"Journ. f. prakt. Chem.," 51, 338.)—Precipitate with ammonia, heat, filter, ignite, weigh. Triturate, and weigh off a portion of the powder, in a small porcelain boat. Insert the latter into a porcelain tube, lying in an horizontal position and having one end closed with a cork into which a narrower open glass tube is fitted. Conduct into the open end hydrogen gas, dried by transmission through sulphuric acid and chloride of calcium. When the air is expelled from the apparatus, heat the porcelain tube gradually to redness, and maintain it at that temperature as long as water forms (about 1 hour). Allow the tube now to cool in a current of hydrogen gas, then remove the little boat, and weigh it. The loss of weight indicates the quantity of oxygen which was combined with the iron to sesquioxide.

If you wish to determine the oxides separately, which may be deemed more particularly necessary if the analysed substance contains much alumina and little sesquioxide of iron, treat the mixture of alumina, sesquioxide of chromium, and metallic iron, with highly dilute nitric acid (1 part of acid to 30 or 40 parts of water), or with water to which very little nitric acid is gradually added. The iron is dissolved, the alumina and sesquioxide of chromium remain undissolved. The latter oxides are weighed; the iron is precipitated from the filtrate by ammonia, after ebullition of the fluid. The results of *Rivot's* experimental analyses were highly satisfactory. The method is more particularly suitable in cases where the quantity of alumina is large, that of sesquioxide of iron small.

β. *Deville* transmits through the tube, after the reduction by hydrogen has been effected as in α, first hydrochloric gas, and then again hydrogen. This leaves the alumina in a state of purity; the iron volatilizes as protochloride, and is either determined in the direct way, or calculated from the loss. If it is intended to do the former, the protochloride in the tubes and in the tubulated receiver is dissolved by heating dilute hydrochloric acid to boiling, and conducting the fumes into the porcelain tube; the tubulature of the receiver is directed downwards in this operation. *Deville* has employed his method simply to effect the separation of sesquioxide of iron from alumina; but it is obvious that it is equally adapted for the separation of sesquioxide of chromium.

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[*] "Annal. der Chem. und Pharm.," 72, 329. *Ebelmen* has given his method simply for the separation of CoO and NiO from MnO.

[†] "Annal der Chem. und Pharm.," 80, 364. *Brunner* has given his method simply for nickel and zinc.

SUPPLEMENT: *Decomposition of Chrome-Iron* (*Rivot*, "Journal f. prakt. Chem.," 51, 347).

Treat the finely levigated mineral as directed in *a*. An hour's application of a bright red heat is sufficient to effect the complete reduction of the protoxide of iron. The mass is allowed to cool in the stream of hydrogen gas, and then digested 24 hours with dilute nitric acid, which dissolves the iron, lime, and magnesia, leaving the sesquioxide of chromium, alumina, and silicic acid undissolved.

b. SESQUIOXIDE OF IRON FROM PROTOXIDE OF IRON.

Compounds containing only sesquioxide and protoxide of iron, or, at all events, besides these two, no other substances liable to undergo alteration by ignition in a stream of hydrogen gas, are accurately weighed, intensely ignited in hydrogen gas, allowed to cool in the gaseous current, and then again weighed; the loss of weight indicates the quantity of oxygen originally combined with the iron. The quantity of iron may be determined, according to circumstances, either by simply weighing the residue, or by an ulterior analysis of the latter. The operation may be conducted either as in *a*, or in a bulb-tube. If, by way of control, you wish to weigh the water generated in the process of reduction, you may use the apparatus described in § 36, and illustrated by Fig. 37. The gasometer is, in that case, to be filled with hydrogen gas instead of atmospheric air. 70

c. PROTOXIDE OF COBALT AND PROTOXIDE OF NICKEL FROM OXIDE OF ZINC.

Ullgren's Method. (*Berzelius's* "Jahresbericht," 21, 145.)

Precipitate the solution with carbonate of soda, in the manner and with the precautions directed in § 108, *a*. Wash the precipitates carefully with boiling water, dry, ignite, and weigh. Triturate finely, introduce a weighed portion of the powder into the bulb of a bulb-tube, and heat the latter to incipient redness, transmitting a slow current of hydrogen gas through it during the operation. As soon as the formation of water ceases, stop the application of heat, and allow the mass to cool in the hydrogen stream. The mass contains the whole of the cobalt and nickel in the metallic state, the whole of the zinc as oxide. Close one end of the tube by fusion, fill up with a concentrated solution of carbonate of ammonia, insert a cork into the other end, keeping the tube for 24 hours at a gentle heat (about 104° F.). The oxide of zinc dissolves completely; the undissolved portion, which consists of the cobalt and nickel, is washed repeatedly with solution of carbonate of ammonia, then dried and weighed. The quantity of the oxide of zinc is found by cautiously evaporating the ammoniacal solution, and igniting the residue. The cobalt invariably retains some alkali. 71

4. *Method based upon the different deportment of the Chlorides of the Metals with Hydrogen at a Red Heat.*

PROTOXIDE OF COBALT AND PROTOXIDE OF NICKEL FROM PROTOXIDE OF MANGANESE.

The oxides are thrown down from the solution; if the latter is free 72 from salts of ammonia, this is effected by precipitating with solution of soda; but in presence of a considerable proportion of salts of ammonia, the best way is to precipitate with sulphide of ammonium, wash the sulphides of the metals thrown down, dissolve in nitrohydrochloric acid, and precipitate with solution of soda.

The precipitated oxides, or a weighed portion of them, are introduced into a bulb-tube, and exposed, in a current of dry hydrochloric gas, to a moderate red heat, until they are completely converted into chlorides, and consequently until the formation of water has entirely ceased, which takes a long time to accomplish. A strong heat is now applied to the bulb, and dry hydrogen gas transmitted over the chlorides until a slight cloud only is perceptible upon approaching a glass rod moistened with ammonia to the mouth of the tube. The protochlorides of nickel and cobalt are reduced to the metallic state in this process, whilst the protochloride of manganese remains unaltered. The mass is allowed to cool in the current of hydrogen gas, and the bulb-tube is then placed in a cylinder with water. The greater part of the protochloride of manganese dissolves, a small portion floating about in the fluid in the form of brown flakes; the cobalt and nickel speedily subside. The fluid, with the suspended light flakes in it, is decanted from the reduced metals, and the latter washed on a weighed filter—first with a little highly dilute hydrochloric acid, then with water—dried, and weighed (compare also § 111, *b*). The decanted fluid, with the washings together with some hydrochloric acid, is concentrated by evaporation, and the manganese precipitated with carbonate of soda (§ 109). The results are accurate (*H. Rose*).

5. *Methods based upon the different capacity of the several Oxides to be converted by Oxidizing Agents into higher Oxides, or by Chlorine into higher Chlorides.*

a. SESQUIOXIDE OF CHROMIUM FROM ALL THE OXIDES OF THE FOURTH GROUP.

Fuse the oxides with nitrate of potassa and carbonate of 73 soda (compare § 157), boil the mass with water, add a sufficient quantity of spirit of wine, and heat gently for several hours. Filter, and determine in the filtrate the chromium as directed § 130, and in the residue the bases of the fourth group. The following is the theory of this process: the oxides of zinc, cobalt, nickel, iron, and partly that of manganese, separate upon fusion with nitrate of potassa and carbonate of soda, whilst, on the other hand, manganate (perhaps also some ferrate) and chromate of potassa are formed. Upon boiling with water, part of the manganic acid of the manganate of potassa is converted into permanganic acid at the expense of the oxygen of the other part, which is reduced to the state of binoxide; the latter separates, whilst the potassa salts are dissolved. The addition of alcohol, with the application of a gentle heat, effects the decomposition of the permanganate of potassa, and the reduction of the permanganic acid to the state of binoxide of manganese, which separates. Upon filtering the mixture, we have therefore now the whole of the chromium in the filtrate as alkaline chromate, and all the oxides of the fourth group on the filter.

The analysis of the native compound of sesquioxide of chromium with protoxide of iron (chrome-iron), requires the most careful elutriation of the mineral, and long-protracted fusion with the proper flux. However, in most cases, even the strictest attention to these points will not prevent part of the mineral remaining undecomposed; in which case the residue left undissolved by water will not completely dissolve in hydrochloric acid. In cases of this kind, the best way is to proceed as follows:—Fuse 8 parts of borax in a platinum crucible, add to the mass in fusion 1 part of the finely pulverized ore, and keep the crucible half an hour longer at a bright red heat; add dry carbonate of soda as long as it causes effervescence, then gradually, and with frequent stirring with a platinum wire, 3 parts of a mixture of equal parts of nitrate of potassa and carbonate of soda, and keep the mass a few minutes longer in fusion. The sesquioxide of chromium is by this process completely converted into chromated alkali, which is then dissolved out by boiling with water. The residue must completely dissolve in hydrochloric acid (*Hart*, "Chem. Gaz.," 1855, 458).

Calvert ("Chem. Gaz.," 1852, p. 280) recommends to effect the decomposition of the chrome-ores, by mixing the finely pulverized minerals with 3—4 parts of soda-lime and 1 part of nitrate of soda, and fusing the mixture for two hours.

b. PROTOXIDE OF MANGANESE FROM ALUMINA, PROTOXIDE OF NICKEL, AND OXIDE OF ZINC (but not from protoxide of cobalt and the oxides of iron).

Gibbs's Method ("Annal. d. Chem. u. Pharm.," 66, 56).—Precipitate the manganese with binoxide of lead, and proceed exactly as for the separation of manganese from magnesia. 74

c. PROTOXIDE OF MANGANESE FROM ALUMINA, PROTOXIDE OF NICKEL, AND OXIDE OF ZINC (but not from protoxide of cobalt and the oxides of iron).

Schiel's Method.*—Conduct chlorine gas into the solution mixed with acetate of soda (see 58, β). Compare also *Rivot*, *Beudant* and *Daguin*, "Compt. rend.," 1853, 835; "Journ. f. prakt. Chem.," 61, 130. 75

d. PROTOXIDE OF COBALT AND PROTOXIDE OF MANGANESE FROM PROTOXIDE OF NICKEL (*H. Rose*, "Pogg. Annal.," 71, 545).

Dilute the hydrochloric acid solution, in a capacious flask, with 1 litre of water to 2 grms. of metallic oxides in the solution, conduct chlorine gas into the flask until the fluid is saturated, and the vacant space in the flask completely filled with the gas; add elutriated carbonate of lime in excess, let the mixture stand in the cold from 12 to 18 hours, taking care to shake repeatedly; then filter the fluid, which contains the whole of the nickel, from the precipitated sesquioxide of cobalt and manganese. 76

Henry has employed bromine instead of chlorine as the oxidizing agent; he obtained satisfactory results. *Denham Smith* recommends addition of a dilute solution of chloride of lime which has been completely decomposed by addition of sulphuric acid, so as to leave no particle of undecomposed hypochlorite (otherwise nickel would be thrown down with the other oxides).

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* "*Sillim.* Journ.," 15, 275. *Schiel* speaks only of the separation of the manganese from iron and nickel; but it is obvious that its separation from alumina and zinc may be effected by the same method.

6. *Method based upon the different deportment of the Succinates of the several Oxides.*

SESQUIOXIDE OF IRON FROM OXIDE OF ZINC, PROTOXIDE OF MANGANESE, PROTOXIDE OF NICKEL, AND PROTOXIDE OF COBALT.

Add to the solution, if not strongly acid, chloride of ammonium, 77 then neutralize with ammonia so as to precipitate a very small portion of the sesquioxide of iron, leaving the greater part in solution; add now a solution of neutral succinate (or benzoate) of ammonia, and filter the fluid from the succinate of sesquioxide of iron; the filtrate contains the other metallic oxides. For the details of the process, see § 113, 1 *c.* With proper care, the separation is complete; the process is more particularly adapted for cases where the relative proportion of the sesquioxide of iron is rather large.

7. *Methods based upon the deportment of neutralized Solutions of the Oxides at boiling heat.*

a. SESQUIOXIDE OF IRON FROM THE PROTOXIDES OF MANGANESE AND NICKEL AND OTHER STRONG BASES.

Mix the dilute solution largely with chloride of ammonium (at 78 least 20 NH_4Cl to 1 of oxide), add highly dilute solution of carbonate of ammonia in small quantities, at last drop by drop, as long as the precipitated iron redissolves, which takes place promptly at first, but more slowly towards the end. As soon as the fluid has lost its transparency, without showing, however, the least trace of a distinct precipitate in it, and fails to recover its clearness after standing some time in the cold, but, on the contrary, becomes rather more turbid than otherwise, the reaction may be considered completed. When this point has been attained, heat slowly to boiling, and keep in ebullition for a short time after the carbonic acid has been entirely expelled. The sesquioxide of iron separates as a basic salt, promptly if the solution was not too highly concentrated. Add now a drop of ammonia, to see whether the iron has been completely thrown down, then some more ammonia, to convert the basic salt of iron, which has a tendency to dissolve upon cooling, into hydrated sesquioxide, and filter. To ensure accurate results, the fluid must not contain more than 3·4 grms. of sesquioxide of iron in the litre, and must be tolerably free from sulphuric acid, since it is difficult in presence of the latter to hit the exact point of saturation. *Herschel* ("Annal. de Chem. et de Phys.," 49, 306); *Schwarzenberg* ("Annal. d. Chem. u. Pharm.," 97, 216).

b. SESQUIOXIDE OF IRON FROM THE PROTOXIDE.

In compounds which dissolve with difficulty in hydrochloric acid, 79 but are decomposed by moderately concentrated sulphuric acid at a temperature below 618·8° F.* *Scheerer* ("Pogg. Annal.," 86, 91, and 93, 448) separates sesquioxide from protoxide of iron, by effecting the solution in an atmosphere of carbonic acid, kept up during the experiment, diluting with pieces of ice free from air, adding carbonate of ammonia until the acid is nearly neutralized, then finely powdered magnesite (but not magnesia alba), and boiling from 10 to 18 minutes. The whole of the sesquioxide of iron is precipitated by this process. The precipitate is washed as in **62**, with water which, after being mixed with some sulphate of ammonia, has been boiled free from air and allowed to cool out of contact of air. *Kobell* ("Annal. d. Chem. u Pharm.," 90, 244) prefers, as dissolving agent, a mixture of 1 vol. of concentrated sulphuric acid, 2 vols. of water, and 1 vol. of strong hydrochloric acid.

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* Upon boiling, protoxide of iron is peroxidized, the sulphuric acid being reduced to sulphurous acid. *Kobell* ("Annal. der Chem. u. Pharm.," 90, 244).

8. *Method based upon the deportment of the Acetates of the Oxides at boiling heat.*

ALUMINA AND SESQUIOXIDE OF IRON FROM PROTOXIDE OF MANGANESE AND OXIDE OF ZINC.

See **57**, *d*, and § 113, 1, *d*. Results satisfactory. **80**

9. *Method based upon the different deportment of the Oxalates of the several Oxides.*

PROTOXIDE OF COBALT FROM SESQUIOXIDE OF IRON.

81 Mix the solution, which must be as neutral as possible, with binoxalate of potassa (or with oxalic acid and a sufficient quantity of carbonate of potassa to leave the reaction only moderately acid), and allow the mixture to stand at rest for 3 or 4 days, shaded from sunlight. The oxalate of protoxide of cobalt separates completely, free from iron. Wash with cold water, ignite in a stream of hydrogen gas, and weigh the metallic cobalt. The results are satisfactory (*H. Rose*).

10. *Method based upon the different deportment of the Nitrites of the several Oxides.*

PROTOXIDE OF COBALT FROM PROTOXIDE OF NICKEL, ALSO FROM PROTOXIDE OF MANGANESE AND OXIDE OF ZINC.

82 The cobalt is precipitated as nitrite of sesquioxide of cobalt and potassa, as directed § 111, 4. The other bases remain in solution (*Fischer*, "Pogg. Annal.," 72, 477; *A. Stromeyer*, "Annal. d. Chem. u. Pharm.," 96, 218).

11. *Methods based upon the different deportment of the several Oxides with Cyanide of Potassium.*

a. ALUMINA FROM OXIDE OF ZINC, PROTOXIDE OF COBALT, AND PROTOXIDE OF NICKEL.

83 Mix the solution with carbonate of soda, add cyanide of potassium in sufficient quantity, and digest in the cold, until the precipitated carbonates of oxide of zinc and protoxide of cobalt and protoxide of nickel are redissolved. Filter the fluid from the undissolved alumina, wash the latter, and remove the alkali which it contains, by redissolving in hydrochloric acid and reprecipitation by ammonia (*Fresenius* and *Haidlen*, "Annal. d. Chem. u. Pharm.," 43, 129).

b. PROTOXIDE OF COBALT FROM PROTOXIDE OF NICKEL.

84 *Liebig's* Method ("Annal. d. Chem. und Pharm.," 65, 244).—Mix the solution of the two oxides, which must be free from other oxides, with hydrocyanic acid, then with solution of potassa, and warm, until the precipitate first formed is completely redissolved. (Cyanide of potassium, free from cyanate, may be used instead of hydrocyanic acid and potassa.) The solution looks reddish-yellow; heat to boiling to remove the free hydrocyanic acid. By this process the double cyanide of cobalt and potassium ($K\,Cy, Co\,Cy$) in the solution is converted, with evolution of hydrogen, into cobalticyanide of potassium,* whilst the double cyanide of nickel and potassium in the solution remains unaltered. Add to the hot solution finely pulverized and elutriated oxide of mercury, and boil. By this operation the whole of the nickel is precipitated partly as sesquioxide partly as protocyanide, the mercury combining with the liberated cyanogen. If the fluid was neutral before the addition of the oxide of mercury, it shows alkaline reaction after boiling with the latter. The precipitate looks greenish at first, or, if the oxide of mercury has been added in excess, yellowish-gray. Wash and ignite. The residue is pure protoxide of nickel.

To determine the cobalt in the filtrate, supersaturate with acetic acid, boil, precipitate the boiling solution with sulphate of copper, keep in ebullition for some time longer, then filter the fluid from the precipitated cobalticyanide of copper ($Cu_3, Co_2\,Cy_6, + 7\,H\,O$); decompose the latter by boiling with solution of potassa, and calculate the quantity of the cobalt from that of the oxide of copper obtained. The following method, recommended by *Wöhler* ("Annal. d. Chem. und Pharm.," 70, 256), is more simple and convenient. The filtrate is nearly neutralized with nitric acid (a slight alkaline reaction is of no consequence), and a perfectly neutral solution of nitrate of suboxide of mercury added; the white precipitate of cobalticyanide of mercury, which contains the whole of the cobalt, may be readily washed, and gives, upon ignition, with free access of air, pure protosesquioxide of cobalt; the reduction of the latter is effected best with hydrogen. See § 111.

Instead of precipitating the nickel with oxide of mercury, proceed as follows: after expelling the free hydrocyanic acid by boiling, let the solution cool, then supersaturate with chlorine, and redissolve the precipitate of cyanide of nickel which forms, by addition of solution of soda or potassa. The chlorine does not act upon the cobalticyanide of potassium, but it decomposes the double cyanide of nickel and potassium, and throws down the whole of the nickel as black peroxide (*Liebig*, "Annal. d. Chem. u. Pharm.," 87, 128).

c. PROTOXIDE OF COBALT FROM OXIDE OF ZINC.

Add to the solution of the two oxides, which must contain some 85 free hydrochloric acid, common cyanide of potassium (prepared after *Liebig's* method), in sufficient quantity to redissolve the precipitate of protocyanide of cobalt and cyanide of zinc which forms at first; then add a little more cyanide of potassium, and boil some time, adding occasionally one or two drops of hydrochloric acid, but not in sufficient quantity to make the solution acid. Mix the solution with hydrochloric acid in an obliquely placed flask, and boil until the cobalticyanide of zinc which precipitates at first is redissolved, and the hydrocyanic acid completely expelled. Add solution of soda or potassa in excess, and boil until the fluid is clear; the solution may now be assumed to contain all the cobalt as cobalticyanide of potassium, and all the zinc as a mixture or compound of oxide of zinc and alkali. Precipitate the zinc by sulphuretted hydrogen (§ 108). Filter, and determine the cobalt in the filtrate as in **84**. The process is simple and the separation complete (*Fresenius* and *Haidlen*).

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* $2\,(Co\,Cy, K\,Cy) + K\,Cy + H\,Cy = (K_3, Co_2\,Cy_6) + H$.

d. PROTOXIDE OF COBALT FROM PROTOXIDE OF MANGANESE.

86 Mix the solution of the two oxides with hydrocyanic acid, then with solution of potassa and soda, and warm the mixture. If the quantity of hydrocyanic acid added was sufficient, the precipitated protocyanide of cobalt redissolves completely, whilst the greater portion of the precipitated protocyanide of manganese remains undissolved. Filter, and treat the filtrate exactly as in **84** (Separation of Cobalt from Nickel). Ignite the two manganese precipitates together. When the oxide of mercury which the second manganese precipitate contains in admixture, has been expelled, there remains protosesquioxide of manganese. This shows that cobalt may be separated also both from nickel and manganese at the same time; in which case the dissolved portion of the manganese is obtained with the protoxide of nickel (Comp. also *Flajolot,* "Journ. f. prakt. Chem.," 61, 110).

e. PROTOXIDE OF NICKEL FROM OXIDE OF ZINC.

87 Mix the concentrated solution of both oxides with an excess of concentrated pure solution of potassa, then with solution of hydrocyanic acid in sufficient quantity to redissolve the precipitate completely; add solution of sulphide of *potassium* (K S), allow the precipitated sulphide of zinc to deposit at a gentle heat, filter, and determine the nickel in the filtrate by heating for some time with fuming hydrochloric acid and nitric acid, or, instead of the latter, with chlorate of potassa, evaporating, and finally precipitating with potassa (*Wöhler,* "Annal. d. Chem. u. Pharm.," 89, 376).

12. *Methods based upon the Volatility of Zinc.*

a. PROTOXIDE OF COBALT AND PROTOXIDE OF NICKEL FROM OXIDE OF ZINC.

88 *Berzelius* ("Jahresbericht," 21, 144) recommends the following method for the absolute separation of cobalt and nickel from zinc. Precipitate with solution of potassa in excess, boil, and filter the fluid, which contains the greater portion of the zinc dissolved in the caustic potassa, from the precipitated hydrate of protoxide of nickel and cobalt, which also contains some of the zinc; wash the precipitate *thoroughly* with boiling water, and determine the zinc in the filtrate as directed § 108. Dry the precipitate, ignite, and weigh; then mix in a porcelain crucible with pure sugar (recrystallized from solution in alcohol), and heat slowly until the sugar is completely carbonized. Place the crucible, with the lid on, in a bath of magnesia in a larger-sized covered clay crucible, and expose for the space of 1 hour to the very highest degree of heat attainable by a wind furnace. This process causes the reduction of the metals: the whole of the zinc present rises in vapor, the nickel and cobalt, mixed with charcoal, remain. Treat the residue with nitric acid, and determine the oxides by precipitating with solution of potassa, and weighing the precipitate. The difference between this weight and that obtained before, shows the quantity of the oxide of zinc which has been thrown down with the other oxides. This method gives very accurate results only in the separation of nickel from zinc (Compare § 111, *b*).

b. ZINC FROM IRON, IN ALLOYS.

89 *Bobierre* states that these alloys may be readily and accurately analysed by igniting them in a stream of hydrogen gas (see **115**).

13. *Methods based upon the Volumetric Determination of one of the Oxides, and the calculation of the other from the difference.*

a. SESQUIOXIDE OF IRON FROM ALUMINA.

Precipitate both oxides with ammonia (§ 105, *a*, and § 113, 1). 90
Dissolve the weighed residue, or an aliquot part of it, by digestion with concentrated hydrochloric acid, or by fusion with bisulphate of potassa and treating with water containing hydrochloric acid; and determine the iron volumetrically as directed § 113, 2. Calculate the alumina from the difference. This method is to be recommended more particularly in cases where the relative proportion of the sesquioxide of iron is small. In the analysis of larger quantities, it is of course much more convenient to divide the solution, by weighing or measuring, into 2 equal portions, and determine in the one the sesquioxide of iron + alumina, in the other the iron. Instead of estimating the iron by volumetric analysis, you may also precipitate it, after addition of tartaric acid and ammonia, with sulphide of ammonium.

b. SESQUIOXIDE OF IRON FROM PROTOXIDE OF IRON (OXIDE OF ZINC, PROTOXIDE OF NICKEL).

α. Determine in a portion of the substance the total amount of 91
the iron as sesquioxide, or by the volumetrical way. Dissolve another portion by warming with hydrochloric acid in a flask through which carbonic acid is conducted, to exclude the air; dilute the solution, and determine the protoxide of iron volumetrically (§ 112, 2, *a*). The difference gives the quantity of the sesquioxide. This convenient and accurate method will probably replace the more complicated methods hitherto employed, to determine protoxide of iron in presence of sesquioxide. If the compound in which sesqui- and protoxide of iron are to be estimated, is only with difficulty decomposed by acids, fuse 1 part of it with 5 or 6 parts of fused borax, in a small retort, connected with a flask containing nitrogen (produced by combustion of phosphorus in the air); an atmosphere of carbonic acid is less suitable. Triturate the fused mass, and dissolve the powder in boiling hydrochloric acid, in an atmosphere of carbonic acid (*Hermann; v. Kobell*). Iron may also be determined volumetrically in presence of oxide of zinc, protoxide of nickel, &c. It is, indeed, often the better way, instead of effecting the actual separation of the oxides, to determine in one portion of the solution the sesquioxide of iron + oxide of zinc or + protoxide of nickel, in another portion the iron alone, and to find the quantity of sesquioxide by the difference. However, this can be done only in cases where the quantity of iron is relatively small.

β. *Bunsen's* method. Fill the little flask *d* (Fig. 65, § 130) two-thirds with fuming hydrochloric acid, and expel the air above by carbonic acid, by throwing some fragments of carbonate of soda into the flask. Weigh a portion of the substance in an open short tube, and in another similar tube a slight excess of bichromate of potassa; drop the two tubes into the flask, attach the evolution tube, and proceed for the rest as directed § 130, *d*, *β*. Of course you will obtain less free iodine than if no protoxide of iron had been dissolved with the chromate of potassa, as a portion of the liberated chlorine goes to convert the protochloride of iron into sesquichloride; each equivalent of iodine obtained less than corresponds to the chromate of potassa used, is calculated as 2 equivalents of protoxide of iron.

If you wish to ascertain the total quantity of iron contained in the analysed substance, dissolve another portion of it in hydrochloric acid in the flask *a* (Fig. 79), and effect the reduction of the sesquioxide of iron to protoxide, by means of a ball of chemically pure zinc, cast on a fine platinum wire. To exclude all access of air, connect the flask, during the ebullition, with the apparatus *b b′* (Fig. 79).

As soon as the colorless condition of the fluid shows that the reduction is completed, cool the flask in cold water, lift the upper cork, throw a few grains of carbonate of soda into the acid, draw the zinc ball up the tube *b*, wash off the fluid adhering to the ball into the flask, and remove *b b′*. Add quickly a weighed slight excess of bichromate of potassa, attach the evolution tube, and proceed for the rest as just directed.

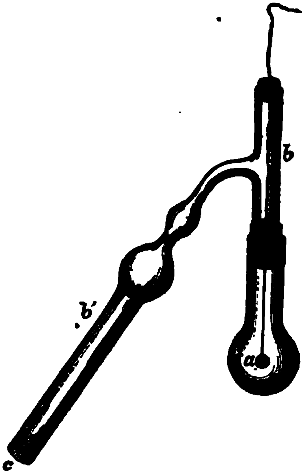

Fig. 79.

c. PROTOXIDE OF MANGANESE FROM ALUMINA AND SESQUIOXIDE OF IRON (*Krieger*, "Annal. d. Chem. u. Pharm.," 87, 261).

Precipitate with carbonate of soda, digest the precipitate some time with the fluid, wash properly, first by decantation, then on the filter, dry, ignite, and determine in a sample the manganese as in **59**. Bear in mind that the precipitate contains the manganese as Mn_3O_4. **92**

d. PROTOXIDE OF MANGANESE FROM OXIDE OF ZINC (*Krieger*).

Precipitate boiling with carbonate of soda, wash the precipitate with boiling water, dry, and ignite. If the analysed substance contained a sufficient quantity of zinc, the precipitate consists of $ZnO + x\,Mn_3O_4$. Weigh off a portion and determine in this the manganese as in **59**.—N.B. If the quantity of zinc is insufficient, proceed as directed **59**. **93**

14. *Indirect Method.*

SESQUIOXIDE OF IRON FROM PROTOXIDE.

Of the many indirect methods proposed, which are now, however, but rarely resorted to since the employment of solution of permanganate of potassa for the volumetric determination of iron, I will only give the following:—Dissolve as in **91**, add solution of sodio-terchloride of gold in excess, close the flask, and allow the reduced gold to deposit; filter the fluid from the gold, and determine the latter as directed § 123. Determine the total quantity of the iron in the filtrate, or in another portion of the substance. The calculation is self-evident: 1 equivalent of gold separated corresponds to 6 **94** equivalents of protochloride or protoxide of iron ($6\ FeCl + AuCl_3 = 3\ Fe_2Cl_3 + Au$). (*H. Rose.*)

IV. SEPARATION OF SESQUIOXIDE OF IRON, ALUMINA, PROTOXIDE OF MANGANESE, LIME, MAGNESIA, POTASSA, AND SODA.

§ 161.

As these oxides are found together in the analysis of most silicates, and also in many other cases, I devote a distinct paragraph to the description of the methods which are employed to effect their separation.

1. *Method based upon the employment of Carbonate of Baryta as Precipitant* (particularly applicable in cases where the mixture contains only a small proportion of lime).

Precipitate the iron—which must be present in the form of sesquioxide—and the alumina by carbonate of baryta,* and separate the two metals, after removing the baryta, by one of the methods given in § 160. Precipitate the manganese from the filtrate, either by yellow sulphide of ammonium, or, after addition of a little hydrochloric acid and saturation with chlorine, by carbonate of baryta, or, as *Gibbs* recommends, by binoxide of lead. If you have used sulphide of ammonium, dissolve the precipitated sulphide of manganese in hydrochloric acid, mix the solution with some sulphuric acid, filter, and determine the manganese as directed § 109, 1, *a*. If you have used carbonate of baryta as precipitant, separate the manganese as directed § 159; if binoxide of lead, proceed as directed § 162. Precipitate the dilute solution now with dilute sulphuric acid, filter, and wash the precipitate until the water running off is no longer rendered turbid by chloride of barium; throw down the lime from the filtrate with oxalate of ammonia, after having previously removed, by means of sulphuretted hydrogen, the last traces of lead, if the binoxide of that metal has been used as precipitant. Filter, evaporate the filtrate to dryness, ignite the residue, and separate the magnesia from the alkalies by one of the methods given in § 153. 95

In cases where the proportion of the alumina is large, that of the iron and manganese small, the solution may be saturated first with chlorine, and the sesquioxide of iron, alumina, and sesquioxide of manganese may then be jointly precipitated by carbonate of baryta, the precipitate dissolved in hydrochloric acid, the baryta thrown down from the solution by the least excess of sulphuric acid, then the three bases by carbonate of soda, and the precipitate *thoroughly* washed, dried, ignited, and weighed; it contains the manganese as Mn_3O_4. If this and the sesquioxide of iron are now determined by the volumetrical method, the difference will give the quantity of the alumina. It will be readily seen that one and the same sample may be used, first, for the determination of the manganese, and then for that of the iron; compare 92 and 90. There is only one objection to this method, namely, that it is apt to give a trifling excess of alumina, as that substance, when precipitated by a fixed alkali, can hardly ever be altogether freed from the latter by washing. The joint precipitation of the alumina, iron, and manganese, may also be effected by ammonia, after previous saturation of the fluid with chlorine, or addition of hypochlorous acid. But, in that case, it is advisable to let the precipitated fluid stand at rest some time in a closed flask, and then to filter with exclusion of air. Care must also be taken to ascertain that the filtrate contains no manganese, which may be known by adding sulphide of ammonium, and allowing it to stand some time.

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* Before adding the carbonate of baryta, it is *absolutely indispensable* to ascertain whether a solution of it in hydrochloric acid is completely precipitated by sulphuric acid, so that the filtrate leaves no residue upon evaporation on platinum.

2. *Method based upon the application of Acetates of the Alkalies as Precipitants.*

Remove from the solution, by evaporation, any very considerable excess of acid which might be present, then dilute again with water, add carbonate of soda,[*] until the fluid is nearly neutral,[†] then acetate of soda, and proceed as in **57**, *d*. Wash the precipitate well, dry, ignite, and weigh. Dissolve in concentrated hydrochloric acid,[‡] and determine the iron by the volumetrical method given in § 113, 2; the difference gives the quantity of the alumina. The filtrate contains the manganese, the alkaline earths, and the alkalies. Precipitate the manganese with chlorine (**58**, β), then the lime with oxalate of ammonia, and the magnesia, lastly, with phosphate of soda. However, if it is intended to estimate the alkalies, the magnesia must be separated as in **18**. This method is convenient, and gives good results. It is often employed in my laboratory. **96**

3. *Method based upon the application of Sulphide of Ammonium as Precipitant.*

Mix with ammonia until a precipitate just begins to form, then add yellowish sulphide of ammonium, allow the precipitate—which contains iron, manganese, and alumina—to subside, and then filter. Separate the lime, magnesia, and alkalies in the filtrate as in **96**. Dissolve the precipitate in hydrochloric acid, and separate the alumina from the iron and manganese by caustic potassa (**64**), and then the iron from the manganese by succinate of ammonia. **97**

The following methods are particularly suitable in cases where no manganese is present, or only inappreciable traces :—

4. *Methods based upon the application of Ammonia as Precipitant.*

a. Precipitate the alumina and sesquioxide of iron with ammonia (see **38**). The precipitate is apt to contain a small admixture of lime, and a somewhat more considerable one of magnesia, whilst, on the other hand, some alumina often remains in solution. Wash by repeated decantation, finally on the filter. Separate the alumina in the precipitate by hydrate of potassa (**64**). Dry the precipitate, which consists principally of hydrated sesquioxide of iron, and ignite; dissolve the residue by digestion with fuming hydrochloric acid, filter, **98** if necessary, from the residuary silicic acid, and then precipitate the sesquioxide of iron by ammonia. Filter, and add the filtrate, which contains a little lime and magnesia, to the first fluid, which contains the bulk of these bases; concentrate strongly, best in a platinum dish, precipitate, by ammonia, the trace of alumina which still remains in solution, and then separate the lime from the magnesia in the filtrate. If it is also intended to estimate the alkalies, the traces of lime and magnesia which have been thrown down with the sesquioxide of iron must be determined separately, as the solution of these two earths generally retains some of the alkali added to effect the separation of the alumina. Manganese, if present, is obtained partly in the precipitate partly in the solution, which tends to interfere with the process. However, by saturating the fluid with chlorine before precipitating by ammonia, the whole of the manganese, at least if present in small proportion only, is obtained in the precipitate.

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[*] In cases where it is intended to estimate the alkalies in the filtrate, carbonate and acetate of ammonia must be used instead of the soda salts.

[†] The addition of the carbonate of soda (or ammonia) must not be continued until a permanent precipitate begins to form.

[‡] A small portion of the precipitate will often remain undissolved; this consists of silicic acid, which must be filtered off, washed, dried, ignited, and weighed.

b. Precipitate the alumina, sesquioxide of iron, and lime, by addition of ammonia and carbonate and oxalate of ammonia, decant, and filter. Dissolve the precipitate in hydrochloric acid, add tartaric acid, to prevent the precipitation of sesquioxide of iron and alumina, and then precipitate the lime with ammonia as oxalate. Filter, and separate the iron from the alumina in the filtrate as in **63**; and the magnesia and alkalies in the first filtrate as in **18**. Should the first filtrate contain sulphuric acid, remove this by chloride of barium, then separate the alkaline earths from the alkalies by evaporation with oxalic acid, ignition, and treating the residue with boiling water, and finally the baryta from the magnesia as in **19**. *Mitscherlich; Lewinstein.* "Journ. f. prakt. Chem.," 68, 99. **99**

c. Wash the ammonia precipitate carefully, dry, and ignite; add, without reducing the residue to powder, at least 10 times the quantity of anhydrous carbonate of soda, cover the crucible, and heat the mixture over the blast gas-lamp or some other appropriate source of heat (the heat of a spirit-lamp with double draught is not sufficiently powerful), until decomposition of the carbonate of soda is no longer observable, at least 45 minutes. Boil the fused mass, best in a silver dish, after addition of some caustic potassa, with water until thoroughly extracted; add, if manganate of soda imparts a green tint to the solution, a few drops of alcohol, and wash the precipitate by decantation and filtration, first with water containing potassa, then with pure water. Dissolve the washed precipitate in hydrochloric acid, heat, with addition of a few drops of alcohol, to facilitate the reduction of the sesquichloride of manganese, and separate finally, by means of acetate of ammonia, the sesquioxide of iron from the manganese, lime, and magnesia contained in the ammonia precipitate, which may then be either separately estimated, or determined jointly with the principal bulk of these alkaline earths. The alumina is determined in the alkaline solution as in **64** (*R. Richter*, "Journ. f. prakt. Chem.," 64, 378). **100**

5. *Method based upon the Decomposition of the Nitrates* (*Deville's* method).

This method presupposes that the bases are combined with nitric acid only. **101**

Proceed first as in **39**. The escape of nitrous acid fumes observed during the heating of the nitrates, is no proof of the total decomposition of the nitrates of sesquioxide of iron and alumina, as these vapors may owe their formation to the conversion of the nitrate of protoxide of manganese into binoxide. Stop the application of heat when no more vapors are evolved, and the substance has acquired a uniform black color. After the treatment with nitrate of ammonia, the solution contains nitrate of lime, nitrate of magnesia, and nitrates of the alkalies, the residue contains alumina, sesquioxide of iron, and binoxide of manganese. That some manganese is dissolved, under certain circumstances, has been stated already in **58**, γ; the small quantity of manganese which has thus got into the solution, is found with the magnesia, and finally separated from the latter.

Deville recommends the following methods to effect the further separation of the bases.

a. Heat the residue with moderately strong nitric acid, until the alumina and sesquioxide of iron are dissolved, leaving the residuary binoxide of manganese of a pure black color. Ignite the residue, and weigh the protosesquioxide of manganese formed. Evaporate the solution in a platinum crucible, ignite, and weigh the mixture of sesquioxide of iron and alumina, which may possibly also contain some protosesquioxide of manganese. Treat a portion of it by the method described in **69**; this gives the weight of the alumina. If manganese was present, the iron cannot be estimated by the difference. *Deville* therefore evaporates the solution of the protochlorides (**69**, β) with sulphuric acid, ignites gently, and treats the residue, which consists of sesquioxide of iron and some sulphate of protoxide of manganese, with water to dissolve the latter. Should the heat applied have been too strong, which might possibly lead to the decomposition also of sulphate of protoxide of manganese, the residue is moistened with a mixture of oxalic acid and nitric acid, some sulphuric acid added, and the process repeated.

b. From the filtrate, precipitate first the lime by oxalate of ammonia, then separate the magnesia from the alkalies as directed § 153, 4. This method is particularly suitable in the absence of manganese.

6. *Method which combines 4 and 5.*

Precipitate with ammonia (**38**), decant, filter, wash, remove the still half-moist precipitate, as far as practicable, from the filter, dissolve the particles still adhering to the latter in nitric acid, transfer this to the dish, to effect also the solution of the bulk of the precipitate; proceed as in **101**, and add the fluid, separated from the sesquioxide of iron and alumina, which still contains small quantities of lime and magnesia, to the principal filtrate. This method is often employed with the best success in my laboratory, in absence of manganese; the determination of the alumina being effected by estimating first the total amount of sesquioxide of iron and alumina, then the sesquioxide of iron separately by the volumetrical method. **102**

Supplement to the Fourth Group.

To § 160 and § 161.

SEPARATION OF SESQUIOXIDE OF URANIUM FROM THE OXIDES OF GROUPS I.—IV.

It has already been stated, in § 114, that sesquioxide of uranium 103 cannot be completely separated from the *alkalies* by means of ammonia, as the precipitated ammonio-sesquioxide of uranium is likely to contain also fixed alkalies. This precipitate should therefore be dissolved in hydrochloric acid, the solution evaporated in a platinum crucible, the residue ignited in a current of hydrogen gas (see Fig. 61, § 111), the chloride of the alkali metals extracted with water, and the protoxide of uranium converted, by ignition in the air, into protosesquioxide.

From *baryta*, sesquioxide of uranium may be separated by sulphuric acid, from *strontia* and *lime*, by sulphuric acid and alcohol. Ammonia fails to effect complete separation of sesquioxide of uranium from the alkaline earths, the uranium precipitate always containing not inconsiderable quantities of the earths.

Sesquioxide of uranium is separated from the *protoxides of nickel,* 104 *cobalt, and manganese, oxide of zinc,* and *magnesia,* by means of carbonate of baryta, added in excess to the fluid, which is allowed to stand in the cold for 24 hours, with occasional stirring (62).

From *alumina* and *sesquioxide of iron,* sesquioxide of uranium may be separated by either of the following methods:

a. Add ammonia to the solution until a precipitate just begins to 105 form, then a sufficient quantity of solution of carbonate of ammonia, which has previously been boiled up once, to destroy any bicarbonate present; dilute with water, and then filter off from the precipitate, which contains the whole of the alumina and sesquioxide of iron. Heat the filtrate cautiously for some time, then supersaturate with hydrochloric acid, which will redissolve the precipitate formed, and precipitate the uranium finally with ammonia, as directed in § 114.

If the solution of carbonate of ammonia is too concentrated, or used in too great excess, or contains bicarbonate, sesquioxide of iron passes into the solution, and the experiment turns out a failure (*H. Rose*).

b. Arendt and *Knop* ("Chem. Centralbl.," 1857, 163) recommend 106 the following method for the separation of sesquioxide of iron from sesquioxide of uranium: Precipitate the two oxides by ammonia, dissolve in acetic acid, add carbonate of ammonia until a precipitate just begins to form, boil, and filter. The precipitate contains the whole of the iron, and some sesquioxide of uranium, which is removed from it by cold digestion with solution of carbonate of ammonia. The same method may be employed also to effect the separation of sesquioxide of uranium from alumina.

FIFTH GROUP.

OXIDE OF SILVER—SUBOXIDE OF MERCURY—OXIDE OF MERCURY—OXIDE OF LEAD—TEROXIDE OF BISMUTH—OXIDE OF COPPER—OXIDE OF CADMIUM.

I. Separation of the Oxides of the Fifth Group from those of the preceding Four Groups.

§ 162.

Index: *Oxide of silver* from the oxides of groups 1—4, 107, 108.
Oxide of mercury from the oxides of groups 1—4, 107, 109.
Suboxide of mercury from the oxides of groups 1—4, 107, 109.
Oxide of lead from the oxides of groups 1—4, 107, 110;—from groups 1 and 2, and from zinc and nickel, 111;—from protoxide of manganese, 118.
Teroxide of bismuth from the oxides of groups 1—4, 107;—from protoxide of manganese, 118.
Oxide of copper from the oxides of groups 1—4, 107, 112, 113;—from oxide of zinc, 114, 115, 116;—from protoxide of manganese, 118.
Oxide of cadmium from the oxides of groups 1—4, 107;—from oxide of zinc, 117;—from protoxide of manganese, 118.

A. *General Method.*

Separation of all the Oxides of the Fifth Group from those of the preceding Four Groups.

Principle: Sulphuretted Hydrogen precipitates from Acid Solutions the Metals of the Fifth Group, but not those of the first Four Groups.

107 The following points require especial attention in the execution of the process:

a. To effect the separation of the oxides of the fifth group from those of the first three groups, by means of sulphuretted hydrogen, it is necessary simply that the reaction of the solution should be acid, the nature of the acid to which the reaction is due being of no consequence. But, to effect the separation of the oxides of the fifth group from those of the fourth, the presence of a free mineral acid is indispensable; otherwise, zinc and, under certain circumstances, also cobalt and nickel may fall down with the sulphides of the fifth group.

β. But even the addition of hydrochloric acid to the fluid will not always entirely prevent the precipitation of the zinc. *Rivot* and *Bouquet* ("Annal. d. Chem. u. Pharm.," 80, 364) declare a complete separation of copper from zinc by means of sulphuretted hydrogen, altogether impracticable. *Calvert* ("Journ. f. prakt. Chem.," 71, 155) states that he has arrived at the same conclusion. On the other hand, *Spirgatis* ("Journ. f. prakt. Chem.," 58, 351) concurs with *H. Rose* in declaring that complete separation of copper from zinc may be effected by means of sulphuretted hydrogen, in presence of a sufficient quantity of free acid.

In this conflict of opinions, I deemed it the wiser course to subject this method once more to a searching investigation. I therefore instructed one of the students in my laboratory, Mr. *Grundmann*, to make a series of experiments in the matter, with a view to settle the question. See Analytical Notes and Experiments, No. 91.

The results obtained proved incontestably that copper may be completely separated from zinc by sulphuretted hydrogen, if the following instructions are strictly complied with.

Add to the copper and zinc solution a copious amount of hydrochloric acid (*e.g.* to 0·2 grm. of oxide of copper in 25 c.c. of solution, 10 c.c. of hydrochloric acid of 1·1 sp. gr.), conduct into the fluid sulphuretted hydrogen largely in excess, filter before the excess of sulphuretted hydrogen has had time to escape or become decomposed, wash with sulphuretted hydrogen water, dry, roast, redissolve in nitrohydrochloric acid, evaporate nearly to dryness, add water and hydrochloric acid as above, and precipitate again with sulphuretted hydrogen. This second precipitate is free from zinc; it is treated as directed in § 119, 1, *a*.

If cadmium is present, a portion of this metal is likely to remain in solution, in presence of the large amount of hydrochloric acid added. It is therefore necessary, in that case, after conducting the sulphuretted hydrogen gas into the fluid, to add saturated sulphuretted hydrogen water until no more sulphide of cadmium precipitates, and then to proceed as for the separation of copper. The separation of cadmium from zinc requires accordingly also a double precipitation with sulphuretted hydrogen, if the quantity of zinc is any way considerable. However, with proper attention to the instructions here given, the method gives perfectly satisfactory results.

γ. The other metals of the fifth group comport themselves in this respect the same as cadmium, *i.e.*, they are not completely precipitated by sulphuretted hydrogen in presence of too much free acid in a concentrated solution. Lead requires the least amount of free acid to be partly retained in solution; then follow in order of succession, cadmium, mercury, bismuth, copper, silver (*M. Martin*, "Journ. f. prakt. Chem.," 67, 371). The separation of these metals from zinc must, therefore, if necessary, be effected by the same process as that of cadmium from zinc (β).

δ. If hydrochloric acid produces no precipitate in the solution, it is preferred as acidifying agent; in the contrary case, sulphuric acid or nitric acid must be used, and the fluid rather largely diluted.

B. *Special Methods.*

SEPARATION OF THE SEVERAL OXIDES OF THE FIFTH GROUP FROM SOME OR ALL OXIDES OF THE FIRST FOUR GROUPS.

1. SILVER is most simply and completely separated from the OXIDES OF THE FIRST FOUR GROUPS by means of hydrochloric acid. 108
The hydrochloric acid must not be used too largely in excess, and the fluid must be sufficiently dilute; otherwise a portion of the silver will remain in solution. Care must be taken also not to omit the addition of nitric acid, which promotes the separation of the chloride of silver. The latter should, under these circumstances, be collected and washed on a filter (§ 115, 1, *a*, β), as washing by decantation would give too large a bulk of fluid.

2. The separation of MERCURY from the METALS OF THE FIRST FOUR GROUPS may be effected also by ignition, which will cause the volatilization of the mercury or the mercurial compound, leaving the non-volatile bodies behind. The method is applicable to alloys as well as to oxides, chlorides, and sulphides. Which of these several methods may be the most appropriate, depends upon the nature of the metals from which the mercury is to be separated, and the selection is accordingly guided by the deportment of the respective compounds. The quantity of mercury is estimated, in this method, either from the loss of weight suffered by the ignited substance, in which case the operation is conducted in a crucible; or the sublimed mercury is collected and weighed as directed § 118, 1, *a*. The best way, where practicable, is to proceed in the manner described in **132** (separation of mercury from silver, &c.). 109

MERCURY IN THE FORM OF SUBOXIDE may also be separated and determined by precipitating with hydrochloric acid (§ 117, 1).

3. FROM THOSE BASES WHICH FORM SOLUBLE SALTS WITH SULPHURIC ACID, OXIDE OF LEAD may be readily separated by that acid. The results are very satisfactory, if the rules given in § 116, 2, are strictly adhered to. 110

If you have lead in presence of baryta, both in form of sulphates, digest the precipitate with a solution of sesquicarbonate of ammonia, without application of heat. This decomposes the lead salt, leaving the baryta salt unaltered. Wash, first with solution of carbonate of ammonia, then with water, and separate finally the carbonate of oxide of lead from the sulphate of baryta, by acetic acid or dilute nitric acid (*H. Rose*, "Journ. f. prakt. Chem.," 66, 166).

From ZINC and NICKEL, as well as from the ALKALIES and ALKALINE EARTHS (but not from sesquioxide of iron and the protoxides of cobalt and manganese), lead may be separated also, by dissolving in acetic acid, adding acetate of soda, heating to 122°–140° F., and conducting chlorine into the fluid. The binoxide of lead separates speedily; as soon as it has separated, the transmission of chlorine is discontinued. The binoxide of lead is washed by decantation, and then filtered (*Rivot*, *Beudant* and *Daguin*, "Journ. f. prakt. Chem.," 61, 136). 111

4. OXIDE OF COPPER FROM ALL OXIDES OF THE FIRST FOUR GROUPS.

a. Acidify the solution with sulphuric acid, and precipitate the copper as subsulphide with *hyposulphite of soda*,* as directed § 119, 1, *c*. The filtrate contains the other bases. Evaporate, with addition of nitric acid, filter, and determine the other oxides in the filtrate.† 112

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* Commercial hyposulphite of soda is often not sufficiently pure; in which case some carbonate of soda must be added to its solution, and the mixture filtered.

† As far back as 1842, *C. Himly* made the first proposal to employ hyposulphite of soda for the precipitation of many metals as sulphides ("Annal. d. Chem. u. Pharm.," 43, 150). The question, after long neglect, has recently been taken up again by *Vohl* ("Annal. d. Chem. u. Pharm.," 96, 237), and *Slater* ("Chem. Gaz.," 1855, 369). *Flajolot*, however, made the first quantitative experiments ("Annal. des Mines," 1853, 641; "Journ. f. prakt Chem.," 61, 105). The results obtained by him are perfectly satisfactory.

It has been stated in § 119, 1, *c*, that the solution of hyposulphite of soda used to precipitate the copper, ought to be free from hydrochloric and nitric acids; however, this is not absolutely necessary; only, in presence of hydrochloric or nitric acid, a much larger proportion of the precipitant is required—in presence of the former, because the subchloride of copper is decomposed only by a large excess of hyposulphite of soda; in presence of the latter, because the precipitant begins to act upon the copper salt only after the decomposition of the nitric acid.

b. The separation is based upon the insolubility of *subiodide of copper* in water slightly acidified with sulphuric or nitric acid, and containing, at the same time, sulphurous acid. 113

As the nitric acid solution generally contains an excess of acid, the latter is removed, in the first place, by evaporation; the fluid is then diluted with water, sulphurous acid added, then solution of iodine in sulphurous acid, in small portions at a time, as long as a precipitate forms (a notable excess would lead to the solution of a little subiodide of copper). The mixture is allowed to stand at rest for 12 hours, then filtered, and the precipitate washed with proper caution to guard against the tendency which the subiodide of copper displays to pass over the rim of the filter. A hole being made in the point of the filter, the washed precipitate is rinsed into a flask by means of water, the filter added, chlorine conducted into the flask, and the solution obtained finally precipitated with hydrate of potassa (§ 119). The other metals are estimated in the fluid filtered off from the subiodide of copper. In presence of iron, a trace of the latter will occasionally fall down with the subiodide of copper. The best way is to separate this after weighing the oxide of copper. *Flajolot* ("Annal. des Mines," 1853, 641; "Journ. f. prakt. Chem.," 61, 105). The results are very satisfactory.

5. OXIDE OF COPPER FROM OXIDE OF ZINC.

a. Precipitate the copper as directed § 119, 3, as sulphosubcyanide; the zinc remains in solution (*Rivot*). 114

b. *Bobierre* ("Compt. Rend," 36, 224; "Journ. f. prakt. Chem.," 58, 380) employed the following method with satisfactory results in the analysis of many alloys of zinc and copper. The alloy is put into a small porcelain boat standing in a porcelain tube, and heated to redness for three-quarters of an hour at the most, a rapid stream of hydrogen gas being conducted over it during the process. The zinc volatilizes, the copper remains behind. Lead also (if that metal be present) is not volatilized in this process. 115

c. As in the separation of copper from zinc by means of sulphuretted hydrogen, the oxide of copper obtained may, under certain circumstances, contain oxide of zinc, I recommend the following process to test the oxide of copper for oxide of zinc, and to remove the latter. When you have weighed the oxide of copper, reduce it by ignition in a stream of hydrogen gas, which is effected best in a porcelain boat inserted in a wide porcelain tube; allow the metallic copper to cool in the stream of hydrogen gas, and when cold, heat for some time with water and hydrochloric acid; filter, wash, conduct a few bubbles of sulphuretted hydrogen into the fluid, to pre- 116 cipitate any traces of copper which might have been dissolved, and determine the zinc as directed § 108, *a.*

d. Rivot and *Bouquet's* method of precipitating the copper from ammoniacal solution by solid hydrate of potassa gives unsatisfactory results, as oxide of zinc always precipitates along with the oxide of copper.

6. OXIDE OF CADMIUM FROM OXIDE OF ZINC.

Prepare a nitric or hydrochloric acid solution of the two metals, 117 as neutral as possible, add a sufficient quantity of tartaric acid, then solution of potassa or soda, until the reaction of the clear fluid is distinctly alkaline. Dilute now with a proper quantity of water, and boil for 1½–2 hours. All the cadmium precipitates as hydrated oxide free from alkali; which is determined as directed § 121, whilst the whole of the zinc remains in solution; the latter metal is determined as directed in § 108, *b. Aubel* and *Ramdohr* ("Annal. d. Chem. u. Pharm.," 103, 33). The results are said to be satisfactory.

7. PROTOXIDE OF MANGANESE FROM OXIDE OF LEAD, TEROXIDE OF BISMUTH, OXIDE OF CADMIUM, AND OXIDE OF COPPER.

If you have a solution containing protoxide of manganese and one 118 of the other bases, precipitate the hot solution with carbonate of soda, wash the precipitate with boiling water, first by decantation, then on the filter, dry, ignite some time, weigh, and determine, in a portion of the residue, the manganese by the volumetrical method (59). If the oxide of lead, of copper, of cadmium, or the teroxide of bismuth, is present in sufficient quantity, the residue has the formula

$$Mn_2O_3 + x\,M\,O.$$

Krieger ("Annal. d. Chem. u. Pharm.," 87, 264). You must never omit adding some sulphide of ammonium to the filtrate, to ascertain whether the oxides have been entirely precipitated by carbonate of soda, since oxide of copper, more especially, is not always completely precipitated by carbonates of the alkalies.

II. SEPARATION OF THE OXIDES OF THE FIFTH GROUP FROM EACH OTHER.

§ 163.

Index: *Oxide of silver* from oxide of copper, 119, 124, 125, 126, 131, 138, 139;—from oxide of cadmium, 119, 124, 126;—from teroxide of bismuth, 119, 123, 126, 134;—from oxide of mercury, 119, 124, 126, 132, 133, 137;—from oxide of lead, 119, 122, 123, 126, 129, 131, 138, 139.

Oxide of mercury from oxide of silver, 119, 124, 126, 132, 133, 137;—from suboxide of mercury, 120;—from oxide of lead, 121, 122, 123, 126, 132, 133, 137;—from teroxide of bismuth, 123, 126, 137;—from oxide of copper, 125, 126, 130, 132, 133, 137;—from oxide of cadmium, 130, 137.

Suboxide of mercury from the oxides of mercury, copper, cadmium, and lead, 120;—from the other metals: see *oxide of mercury*.

Oxide of lead from oxide of silver, 119, 122, 123, 126, 129, 131, 138, 139;—from oxide of mercury, 121, 122, 123, 126, 132, 133;—from oxide of copper, 121, 122, 123, 126, 135;—from teroxide of bismuth, 121, 122, 134, 140;—from oxide of cadmium, 122, 123, 126.

Teroxide of bismuth from oxide of silver, 119, 123, 126, 134;—from oxide of lead, 121, 122, 134, 140;—from oxide of copper, 123, 126, 127, 134;—from oxide of cadmium, 123, 126, 136;—from oxide of mercury, 123, 126, 137.

Oxide of copper from oxide of silver, 119, 124, 125, 126, 131, 138, 139;—from oxide of lead, 121, 122, 123, 126, 135;—from teroxide of bismuth, 123, 126, 127, 134;—from oxide of mercury, 125, 126, 130, 132, 133, 137;—from oxide of cadmium, 125, 126, 128.

Oxide of cadmium from oxide of silver, 119, 124, 126;—from oxide of lead, 122, 123, 126;—from teroxide of bismuth, 123, 126, 136;—from oxide of copper, 125, 126, 128;—from oxide of mercury, 130, 137.

1. *Methods based upon the Insolubility of certain Metallic Chlorides in Water or Spirit of Wine.*

a. OXIDE OF SILVER FROM OXIDE OF COPPER, OXIDE OF CADMIUM, TEROXIDE OF BISMUTH, OXIDE OF MERCURY, AND OXIDE OF LEAD. **119**

α. To separate *oxide of silver* from *oxide of copper*, *oxide of cadmium*, and *teroxide of bismuth*, add to the nitric acid solution hydrochloric acid as long as a precipitate forms, and separate the precipitated chloride of silver from the other oxides in the solution as directed § 115, 1, *a*.

β. The separation of *silver* from *oxide of mercury* is effected in the same way, with this modification, that the fluid is precipitated with solution of chloride of sodium, after previous addition of acetate of soda or acetate of ammonia. If this addition is neglected, the solution does not clear after the precipitation (*Levol*); moreover, some chloride of silver remains in solution, as that salt dissolves in considerable quantity in solution of nitrate of oxide of mercury (*Wackenroder*, *Liebig*). "Ann. der Chem. und Pharm.," 81, 128.

γ. In the separation of *silver* from *lead*, the precipitation is also preceded by addition of acetate of soda. The fluid must be hot and the hydrochloric acid rather dilute; no more must be added of the latter than is just necessary. In this manner, the separation may be readily effected, since chloride of lead dissolves in acetate of soda (*Anthon*). The lead is thrown down from the filtrate by sulphuretted hydrogen.

δ. The volumetrical method (§ 115, 5) is usually resorted to in the mint, to determine the *silver* in *alloys*. In presence of mercury, acetate of soda is added to the fluid, immediately before the addition of the solution of chloride of sodium (see *β*).

b. SUBOXIDE OF MERCURY FROM OXIDE OF MERCURY, OXIDE OF COPPER, OXIDE OF CADMIUM, AND OXIDE OF LEAD.

Mix the highly dilute cold solution with hydrochloric acid, as long **120** as a precipitate (subchloride of mercury) forms; allow this to deposit, filter on a weighed filter, dry at 212° F., and weigh. The filtrate contains the other oxides. If you have to analyse a solid compound of the oxides, insoluble in water, either treat directly, in the cold, with dilute hydrochloric acid, or dissolve in highly dilute nitric acid, and mix the solution with a large quantity of water before proceeding to precipitate. Care must always be taken to effect the solution in a manner excluding the chance of a conversion of the suboxide of mercury into oxide.

c. OXIDE OF LEAD FROM OXIDE OF MERCURY, OXIDE OF COPPER, AND TEROXIDE OF BISMUTH.

Mix the concentrated nitric acid solution with hydrochloric acid in excess, add a large quantity of strong alcohol and some ether, and proceed generally as directed § 116, 4. Heat the filtrate until the alcohol is expelled, and precipitate the metals by sulphuretted hydrogen. **121**

2. *Method based upon the Insolubility of Sulphate of Oxide of Lead.*

OXIDE OF LEAD FROM ALL OTHER OXIDES OF THE FIFTH GROUP.

Mix the nitric acid solution with pure sulphuric acid in excess, evaporate until the sulphuric acid begins to volatilize, allow the fluid to cool, add water (in which, if there is a sufficient quantity of free sulphuric acid present, even the sulphates of oxide of mercury and of teroxide of bismuth dissolve completely), and then filter the solution, which contains the other oxides, *without delay* from the undissolved sulphate of oxide of lead. Wash the latter with water containing sulphuric acid, then finally with spirit of wine, dry, and weigh (§ 116, 2). Precipitate the other oxides from the filtrate by sulphuretted hydrogen. Sulphate of oxide of silver being difficultly soluble, this method cannot be recommended in presence of oxide of silver in notable quantity. **122**

3. *Methods based upon the different Deportment of the several Oxides and Sulphides, with Cyanide of Potassium* (*Fresenius* and *Haidlen*, "Annal. der Chem. und Pharm.," 43, 129).

a. OXIDE OF LEAD AND TEROXIDE OF BISMUTH FROM ALL OTHER OXIDES OF THE FIFTH GROUP.

Mix the *dilute* solution with carbonate of soda in *slight* excess, add solution of cyanide of potassium (free from sulphide of potassium), heat gently for some time, filter, and wash. On the filter you have carbonate of oxide of lead and of teroxide of bismuth, mixed with alkali; the filtrate contains the other metals as cyanides in combination with cyanide of potassium. The method of effecting their ulterior separation will be learnt from what follows. **123**

b. OXIDE OF SILVER FROM OXIDE OF MERCURY, OXIDE OF COPPER, AND OXIDE OF CADMIUM.

Add to the solution, which, if it contains much free acid, must previously be nearly neutralized with soda, cyanide of potassium until the precipitate which forms at first is redissolved. The solu- **124** tion contains the cyanides of the metals in combination with cyanide of potassium as soluble double salts. Add dilute nitric acid in excess, which effects the decomposition of the double cyanides; the insoluble cyanide of silver precipitates permanently, whilst the cyanide of mercury remains in solution, and the cyanides of copper and cadmium, which first fall down, redissolve in the excess of nitric acid. Treat the cyanide of silver as directed § 115, 3. If the filtrate contains only mercury and cadmium, precipitate at once with sulphuretted hydrogen, which completely throws down the sulphides of the two metals; but if it contains copper, you must first evaporate with sulphuric acid, until the odor of hydrocyanic acid is no longer perceptible, and then precipitate with sulphuretted hydrogen, or precipitate at once with solution of potassa or soda (§ 119, 1).

c. OXIDE OF COPPER FROM OXIDE OF SILVER, OXIDE OF MERCURY, AND OXIDE OF CADMIUM.

Mix the solution, as in *b*, with cyanide of potassium until the precipitate which is first thrown down redissolves; add some more cyanide of potassium, then sulphuretted hydrogen water or sulphide of ammonium, as long as a precipitate forms. The sulphides of silver, cadmium, and mercury are completely thrown down, whilst the copper remains in solution, as sulphide dissolved in cyanide of potassium. Allow the precipitate to subside, decant repeatedly, treat the precipitate, for security, once more with solution of cyanide of potassium, heat gently, filter, and wash the sulphides of the metals. To determine the copper in the filtrate, evaporate the latter, with addition of nitric acid and sulphuric acid, until there is no longer any odor of hydrocyanic acid perceptible, and then precipitate with solution of potassa or soda (§ 119, 1). 125

d. ALL THE METALS OF THE FIFTH GROUP FROM EACH OTHER.

Mix the dilute solution with carbonate of soda, then with cyanide of potassium in excess, digest some time at a gentle heat, and filter. On the filter you have carbonate of lead and of teroxide of bismuth, mixed with alkali; separate the two metals by the proper method. Add to the filtrate dilute nitric acid in excess, and filter the fluid from the precipitated cyanide of silver, which determine as directed § 115, 3. Neutralize the filtrate with carbonate of soda, add cyanide of potassium, and conduct into the fluid sulphuretted hydrogen in excess. Add now some more cyanide of potassium, to redissolve the sulphide of copper which may have fallen down, and filter the fluid, which contains the whole of the copper, from the precipitated sulphide of mercury and sulphide of cadmium. Determine the copper as directed in *c.*, and separate the mercury and cadmium as in 130 or 137. 126

4. *Methods based upon the Solubility of some of the Oxides in Ammonia or Carbonate of Ammonia.*

a. OXIDE OF COPPER FROM TEROXIDE OF BISMUTH.

a. Mix the nitric acid solution with carbonate of ammonia in excess. The bismuth separates as carbonate of teroxide, whilst the carbonate of copper is redissolved by the excess of carbonate of ammonia. 127

As the precipitate, however, generally retains a little copper, it is necessary to redissolve it, after washing, in nitric acid, and precipitate again with carbonate of ammonia; the same operation must be repeated a third time if required. Some solution of carbonate of ammonia may be added to the water used for washing the precipitate. Apply heat to the filtrate that the carbonate of ammonia may volatilize (adding finally some ammonia), and determine the copper as directed § 119, 1, *a*, *β*. With the repeated precipitation here recommended, this method gives perfectly accurate results. (Comp. also *R. Schneider*, "Journ. f. prakt. Chem.," 60, 311.)

β. Mix the solution with some chloride of ammonium, and drop it gradually into dilute solution of ammonia. The bismuth is precipitated as a basic salt, whilst the oxide of copper remains in solution as an ammoniacal double salt (*Berzelius*). Wash the precipitated salt of bismuth with dilute solution of ammonia, dissolve in dilute nitric acid, and determine the bismuth as directed § 120. Determine the copper in the ammoniacal solution as directed § 119, 1, *a*, *β*. In this method, also, it is advisable to precipitate twice, as in *a*.

b. OXIDE OF COPPER FROM OXIDE OF CADMIUM.

Add carbonate of ammonia in excess. Carbonate of oxide of cadmium separates, whilst the oxide of copper remains in solution with some oxide of cadmium. Upon exposure to air, the latter separates, the former remaining in solution (*Stromeyer*). Treat the solution as in **127**. The process is more convenient than **125**, but the separation is less complete. **128**

c. CHLORIDE OF LEAD AND CHLORIDE OF SILVER may be separated also by solution of ammonia, which dissolves the latter, leaving the former undissolved as basic chloride of lead. Bear in mind that the chloride of silver must be recently precipitated, and the light carefully excluded during the process. The chloride of silver is thrown down from the ammoniacal solution by nitric acid. It is necessary to test the fluid filtered from the chloride of silver with sulphuretted hydrogen to ascertain whether ponderable quantities of chloride of silver may not be retained in solution by the agency of the ammonia salts. **129**

5. *Methods based upon the Reduction of some of the Oxides or Chlorides by Formate of Soda.*

a. OXIDE OF MERCURY FROM OXIDE OF COPPER AND OXIDE OF CADMIUM.

Mix the solution with hydrochloric acid, if not already present, nearly saturate with soda, and precipitate the mercury with formate of soda as directed § 118, 2. The copper and cadmium in the filtrate are separated and determined by the proper method. **130**

b. OXIDE OF SILVER FROM OXIDE OF COPPER AND OXIDE OF LEAD.

Saturate the solution with soda, add an alkaline formate, and apply heat until the evolution of carbonic acid ceases. The whole **131** of the silver separates in the metallic state, the oxide of copper and oxide of lead remain in solution (*H. Rose*).

6. *Methods based upon the Volatility of some of the Metals, Oxides, or Chlorides, at a high Temperature.*

a. MERCURY FROM SILVER, LEAD, COPPER (in general from the metals forming non-volatile chlorides). 132

The process is conducted in the apparatus illustrated by Fig. 80.

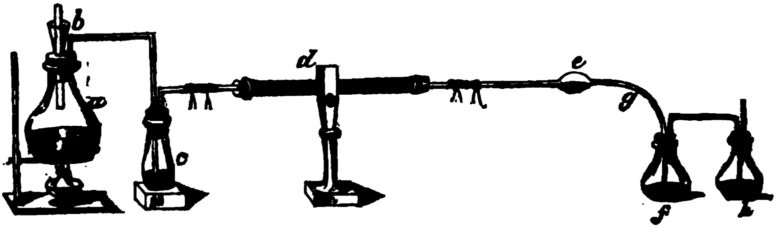

Fig. 80.

Precipitate with sulphuretted hydrogen, collect the precipitated sulphides on a weighed filter, dry at 212°, and weigh. Introduce an aliquot part of the dry precipitate into the bulb *e*; transmit a slow stream of chlorine gas through the tube,[*] and apply a gentle heat to the bulb, increasing this gradually to faint redness. First chloride of sulphur distils over, which decomposes with the water in the flasks *f* and *h* (§ 148, II., 1, *c*); then the chloride of mercury formed volatilizes, condensing partly in the flask *f*, partly in the hind part of the tube *g*. Cut off that part of the tube, rinse the sublimate with water into the flask *f*, and add to the contents of the latter also the water in *h*. Warm the solution until the smell of chlorine is gone off, and then determine in the fluid filtered from the sulphur which may still remain undissolved, the mercury as directed § 118. If the residue consists of silver alone, or of lead alone, you may weigh it at once; but if it contains several metals, you must reduce the chlorides by ignition in a stream of hydrogen gas, and dissolve the reduced metals in nitric acid, for their ulterior separation. Bear in mind that, in presence of lead, the sulphides and the chlorides of the metals must be heated *gently*, the former in a stream of chlorine, the latter in a stream of hydrogen gas, otherwise some chloride of lead might volatilize.

If it is intended to determine the mercury by the difference, instead of in the direct way, the apparatus may be much simplified. An aliquot part of the weighed sulphides is weighed in a porcelain boat, which is inserted into a tube; a current of chlorine is transmitted through the latter, and heat applied; by which means complete expulsion of the sulphur and mercury is effected. If silver or lead alone was present with the mercury, the chloride of silver or chloride of lead remaining in the boat is weighed at the end of the process, and the part calculated upon the whole, which gives the quantity of the silver or lead, and accordingly also that of the sulphide of silver or sulphide of lead in the weighed precipitate of the 133 mixed sulphides, and the difference will consequently give the quantity of sulphide of mercury contained in the precipitate of the mixed sulphides. The results are accurate.

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[*] See § 148, II., 1, *c*, foot note.

In alloys, the mercury may often be determined simply from the loss which the analysed substance suffers by ignition.

b. TEROXIDE OF BISMUTH FROM OXIDE OF SILVER, OXIDE OF LEAD, AND OXIDE OF COPPER.

The separation is effected exactly in the same way as that of mercury from the same metals (**132,133**). The method is more especially convenient for the separation of the metals in alloys. Care must be taken not to heat too strongly, as otherwise chloride of lead might volatilize; nor to discontinue the application of heat too soon, as otherwise bismuth would remain in the residue. If it is intended to determine the bismuth in the direct way, water containing hydrochloric acid is poured into the flasks *f* and *h*, and the bismuth determined as directed in § 120. **134**

7. *Method based upon the Peroxidation of Lead by Chlorine.*

LEAD FROM COPPER.

Proceed as for the separation of lead from zinc and nickel (**111**). **135**

8. *Method based upon the different Deportment of the Chromates.*

BISMUTH FROM CADMIUM.

Precipitate the bismuth as directed § 120, 2. The filtrate contains the whole of the cadmium. Concentrate by evaporation, and then precipitate the cadmium by the cautious addition of carbonate of soda, as directed § 121, 1, *a.*, *Jul. Löwe* ("Journ. f. prakt. Chem.," 67, 469); *W. Pearson* ("Phil. Mag.," xi. 204). The results are said to be satisfactory. **136**

9. *Method based upon the different Deportment of the several Sulphides with Nitric Acid.*

OXIDE OF MERCURY FROM SILVER, BISMUTH, COPPER, CADMIUM, AND LEAD.

Boil the thoroughly washed precipitated sulphides with perfectly pure moderately dilute nitric acid. The sulphide of mercury is left undissolved, the other sulphides are dissolved. Absence of chlorine is indispensable. *G. v. Rath* ("Pogg. Ann.," 96, 322; "Journ. f. prakt. Chem.," 66, 479) employed this method, which is so universally used in qualitative analysis, with perfect success for the separation of mercury from bismuth. It is less suitable for the separation of mercury from lead. **137**

10. *Separation of Silver by Cupellation.*

CUPELLATION was formerly the universal method of determining SILVER in alloys with COPPER, LEAD, &c. The alloy is fused together with a sufficient quantity of pure lead to give to 1 part of silver, 16 to 20 parts of lead, and the fused mass is heated, in a muffle, in a small cupel made of compressed bone-ash. Lead and copper are oxidized, and the oxides absorbed by the cupel, **138** the silver being left behind in a state of purity. One part by weight of the cupel absorbs the oxide of about 2 parts of lead; the quantity of the sample to be used in the experiment may be estimated accordingly. This method is only rarely employed in laboratories; I have given it a place here, however, because it appears to be the safest process to determine very small quantities of silver in alloys. (Compare *Malaguti*, and *Durocher*, "Comptes rend.," 29, 689. *Dingler*, 115, 276.)

11. *Volumetric Determination of Silver in Presence of Lead and Copper: Method based upon the Deportment of Nitrate of Silver with Solution of Iodide of Starch.*

Prepare a solution of iodide of starch in water, and determine the strength by its action upon 10 c.c. of a neutral centesimal-equivalent solution of nitrate of silver (1·0797 grm. of silver in the litre), which has previously been mixed with some precipitated pure carbonate of lime. If 10 c.c. of the silver solution require 50 to 60 c.c. of the iodide of starch solution, the latter may be considered of the proper degree of concentration. Upon adding the iodide of starch solution to the solution of nitrate of silver, the color imparted disappears quickly at first, and the fluid becomes yellowish, owing to the formation of iodide of silver. Discontinue adding iodide of starch solution as soon as the fluid has acquired a bluish-green tint. There is no difficulty in hitting the exact point when the reaction is completed. The carbonate of lime not only serves to neutralize the free acid, but facilitates also the perception of the change of color. To analyse an alloy of silver with copper, dissolve about 0·5 grm. of it in nitric acid, and dilute to 100 c.c., to lessen the color of the copper; saturate 5 c.c. of this solution with carbonate of lime, and add iodide of starch until the fluid acquires a bluish-green tint. Or determine very approximately the silver in 2 c.c. of the solution, then precipitate from 50 c.c. of this, almost the whole of the silver (about 99 per cent.) with solution of chloride of sodium of known strength, filter (as chloride of silver also exercises a decolorizing action), and then determine the rest of the silver by means of iodide of starch. If the quantity of silver to be determined exceeds 0·020 grm., the latter is always the safer way. If you have a nitric acid solution of silver and lead, precipitate the lead with sulphuric acid, filter, add carbonate of lime to the filtrate until the free acid is neutralized, filter again if necessary, add more carbonate of lime, and then solution of iodide of starch. Highly dilute solutions must be concentrated, as the quantity operated upon should never exceed 50 or at the very highest 100 c.c. Salts of mercury must not be present, as these act upon iodide of starch analogously to salts of silver. *F. Pisani* ("Ann. des Mines," x. 83; *Liebig* and *Kopp's* "Jahresber," 1856, 749). This method gives quite satisfactory results; it is particularly suitable for the estimation of small quantities of silver. 139

12. *Precipitation of one Metal by another in the Metallic State.*

OXIDE OF LEAD FROM TEROXIDE OF BISMUTH.

Precipitate the solution with carbonate of ammonia, wash the 140 precipitate, and dissolve in acetic acid, in a stoppered flask; place a weighed rod of pure lead upright in the solution and nearly fill up with water, so that the rod is entirely covered by the fluid; insert the stopper, and let the flask stand at rest for about 12 hours, with occasional shaking. Wash the precipitated bismuth off from the lead rod, collect on a filter, wash, and dissolve in nitric acid; evaporate the solution, and determine the bismuth as directed § 120. Determine the lead in the filtrate as directed § 116. Dry the leaden rod, and weigh; subtract the loss of weight which the rod has suffered in the process, from the amount of the lead produced from the filtrate (*Ullgren*).

SIXTH GROUP.

TEROXIDE OF GOLD—BINOXIDE OF PLATINUM—PROTOXIDE OF TIN—BINOXIDE OF TIN—TEROXIDE OF ANTIMONY (ANTIMONIC ACID)—ARSENIOUS ACID—ARSENIC ACID.

I. SEPARATION OF THE OXIDES OF THE SIXTH GROUP FROM THE OXIDES OF THE FIRST FIVE GROUPS.

§ 164.

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Tin from the oxides of groups, I. and II., 141, 149, 152.
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„ cobalt, 141, 143, 148, 149, 151.
„ iron, 141, 143, 148.
„ silver, 142, 143, 148, 151.
„ mercury, 142, 143, 148.
„ lead, 142, 143, 148, 151.
„ copper, 142, 143, 148, 149, 151.
„ bismuth, 142, 143, 148.
„ cadmium, 142, 143, 148.

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„ manganese, 141, 143, 150.
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„ nickel, 141, 143, 151, 155, 157, 158, 159, 160, 161.
„ cobalt, 141, 143, 151, 155, 157, 158, 159, 160, 161.
„ iron, 141, 143, 154, 155, 156, 159, 160.
„ silver, 142, 143, 151, 155, 160.
„ mercury, 142, 143, 155, 160.
„ lead, 142, 143, 151, 155, 158, 160, 163.
„ copper, 142, 143, 151, 155, 156, 158, 160, 164, 165.
„ bismuth, 142, 143, 155, 160.
„ cadmium, 142, 143, 155, 158, 160.

A. *General Methods.*

1. *Method based upon the Precipitation of the Oxides of the Sixth Group from Acid Solutions by Sulphuretted Hydrogen.*

ALL OXIDES OF THE SIXTH GROUP FROM THOSE OF THE FIRST FOUR GROUPS.

Conduct into the acid* solution sulphuretted hydrogen in excess, and filter from the precipitated sulphides (corresponding to the oxides of the sixth group). 141

The points mentioned § 162 (**107**, α, β, and γ) must also be attended here. As regards γ, antimony and tin are to be inserted between cadmium and mercury, in the order of metals there given. With respect to the exceptional conditions required to secure the complete precipitation of certain metals of the sixth group, I refer to Section IV. I have to remark in addition.

α. That sulphuretted hydrogen fails to separate arsenic acid from oxide of zinc, as, even in presence of a large excess of acid, the whole or at least a portion of the zinc precipitates with the arsenic as Zn S, As S_5 (*Wöhler*). To secure the separation of the two bodies in a solution, the arsenic acid must first be converted into arsenious acid, by heating with sulphurous acid, before the sulphuretted hydrogen is conducted into the fluid.

β. That in presence of antimony, tartaric acid is advantageously added if oxides of the fourth group alone are present, which may be thrown down from the filtrate, after addition of ammonia, by sulphide of ammonium; but that it had better be omitted in the analysis of compounds containing alumina, alkaline earths, and alkalies. In the case of such compounds, sulphuretted hydrogen is conducted into the clear hydrochloric acid solution, water is then added, sulphuretted hydrogen again conducted into the fluid, a further quantity of water added, and the precipitation completed by conducting a sufficient amount of sulphuretted hydrogen into the fluid.

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* Hydrochloric acid answers best as acidifying agent.

2. *Methods based upon the Solubility of the Sulphides of the Metals of the Sixth Group in Sulphides of the Alkali Metals.*

a. The Oxides of Group VI. (with the exception of Gold and Platinum) from those of Group V. 142

Precipitate the acid solution with sulphuretted hydrogen, paying due attention to the directions given in Section IV. under the heads of the several metals, and also to the remarks in **141**. The precipitate consists of the sulphides of the metals of groups V. and VI. Wash, treat immediately after with yellow sulphide of ammonium, and digest the mixture for some time at a gentle heat; filter off the clear fluid, treat the residue again with sulphide of ammonium, digest a short time, repeat the same operation, if necessary, a third and fourth time, filter, and wash the residuary sulphides of group V. with water containing sulphide of ammonium. If protosulphide of tin is present, some flowers of sulphur must be added to the sulphide of ammonium, unless the latter be very yellow. In presence of copper, the sulphide of which is a little soluble in sulphide of ammonium, sulphide of sodium should be used as solvent. However, this substitution can be made only in the absence of mercury, since the sulphides of that metal are soluble in sulphide of sodium.

Add to the alkaline filtrate, gradually, hydrochloric acid in small portions, until the acid predominates; allow to subside, and then filter the fluid from the precipitate, which consists of the sulphides of the metals of the sixth group, mixed with some sulphur.

Schneider ("Annal. d. Chem. u. Pharm.," 101, 64) states that he failed in effecting complete separation of tersulphide of bismuth from bisulphide of tin by digestion with sulphide of potassium, but succeeded in accomplishing that object, by conducting sulphuretted hydrogen into the potassa solution of tartrate of teroxide of bismuth and protoxide of tin (which decompose into suboxide of bismuth and binoxide of tin).

b. The Oxides of Group VI. (with the exception of Gold and Platinum) from those of Groups IV. and V. 143

a. Neutralize the solution with ammonia, and add yellow sulphide of ammonium in excess; cover the vessel, allow the mixture to digest some time at a moderate heat, and then proceed as in **142**. Repeated digestion with fresh quantities of sulphide of ammonium is indispensable. On the filter, you have the sulphides of the metals of groups IV. and V. Wash with water containing sulphide of ammonium.

In presence of nickel, this method offers peculiar difficulties. In presence of copper (and absence of mercury), soda and sulphide of sodium are substituted for ammonia and sulphide of ammonium.*

β. In the analysis of solid compounds (oxides or salts), it is in most cases preferable to fuse the substance with 3 parts of dry carbonate of soda and 3 of sulphur, in a covered porcelain crucible, over a lamp. When the contents are completely fused, and the excess of sulphur is volatilized, the mass is allowed to cool, and then treated with water, which dissolves the sulphur salts of the metals of the sixth group, leaving the sulphides of groups IV. and V. undissolved. By this means, even ignited binoxide of tin may be tested for iron, &c., and the amount of the admixture determined (*H. Rose*). The solution of the sulphur salts is treated as in **142**.

B. *Special Methods.*

1. *Methods based upon the Insolubility of some Metals of the Sixth Group in Acids.*

a. GOLD FROM METALS OF GROUPS IV. AND V. IN ALLOYS.

a. Heat the alloy with pure nitric acid, or, according to circum- **144** stances, with hydrochloric acid. The other metals dissolve, the gold is left. The alloy must be reduced to filings, or rolled out into thin sheets. Alloys of gold containing silver or lead, or both, can be analysed by this method only if the quantity of the two latter metals, or of either, amounts to more than 80 per cent., otherwise the silver and lead are not completely dissolved. Alloys of silver and gold containing less than 80 per cent. of silver, are therefore fused together with 3 parts of lead, before they are treated with nitric acid. The residuary gold is weighed; but its purity must be ascertained, by dissolving in cold dilute nitrohydrochloric acid, not in concentrated hot acid, as chloride of silver also is soluble in the latter.

At the Mint Conference held at Vienna, in 1857, the following process was agreed upon for the mints in the several states of Germany. Add to 1 part of gold supposed to be present, 2½ parts of pure silver, wrapped up in paper, and introduce into a cupel in which the requisite amount of lead is just fusing.† After the removal of the lead (by absorption), the button of gold and silver is flattened, by hammering or rolling, then ignited, and rolled; then treated first with nitric acid of 1·2 sp. gr., afterwards with nitric acid of 1·3 sp. gr. Lastly, it is washed, ignited, and weighed ("Kunst und

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* The hitherto universally admitted accuracy of this method has lately been called in question by *Bloxam* ("Ann. d. Chem. und Pharm.," 83, 204). That chemist found that sulphide of ammonium fails to separate small quantities of bisulphide of tin from large quantities of sulphide of mercury and sulphide of cadmium (1 : 100); and that more especially the separation of copper from tin and antimony (also from arsenic) by this method is a failure, as nearly the whole of the tin remains with the copper. On the other hand, however, Mr. *Lucius*, one of the students in my laboratory, has succeeded in effecting complete separation of copper from tin by means of yellowish sulphide of sodium. But it is indispensable to digest three or four times with sufficiently large quantities of the solvent, as stated in the text.

† If the weighed sample, say 0·25 grm., contains 98–92 per cent. of gold, 3 grms. of lead are required; if 92–87·5, 4 grms.; if 87·5–75, 5 grms.; if 75–60, 6 grms.; if 60–35, 7 grms.; if less than 35, 8 grms.

Gewerbeblatt f. Baiern," 1857, 151; "Chem. Centralbl.," 1857, 307; "Polyt. Centralbl.," 1857, 1151, 1471, 1639).

β. Heat the finely divided (filed or rolled) alloy in a capacious platinum dish with concentrated pure sulphuric acid until the evolution of gas has ceased, and the sulphuric acid begins to volatilize; or fus the alloy with bisulphate of potassa (*H. Rose*). Separate the gold from the sulphates of the metals, by treating the mass first with cold, finally with boiling water. It is advisable to repeat the operation with the separated gold, and ultimately test the purity of the latter.

b. PLATINUM FROM OTHER METALS OF GROUPS IV. AND V., IN ALLOYS.

145 The separation is effected by treating the substance with sulphuric acid or, better still, with bisulphate of potassa; but not with nitric acid, as platinum in alloys will, under certain circumstances, dissolve in that acid.

2. *Method based upon the Separation of Gold in the metallic state.*

GOLD FROM ALL OXIDES OF GROUPS I.—V., with the exception of OXIDE OF LEAD AND OXIDE OF SILVER.

146 Precipitate the hydrochloric acid solution with oxalic acid as directed § 123, *b*, γ, and filter off the gold when it has completely separated. Take care to add a sufficient quantity of hydrochloric acid to prevent oxalates insoluble in water precipitating along with the gold, for want of a solvent.

3. *Method based upon the Precipitation of Platinum as Potassio- or Ammonio-Bichloride of Platinum.*

PLATINUM FROM THE OXIDES OF GROUPS IV. AND V., with the exception of LEAD AND SILVER.

147 Precipitate the platinum with chloride of potassium or chloride of ammonium as directed § 124, and wash the precipitate thoroughly with spirit of wine.

4. *Methods based upon the Separation of Oxides insoluble in Nitric Acid.*

a. TIN FROM METALS OF GROUPS IV. AND V. IN ALLOYS.

148 Treat the finely divided alloy with nitric acid as directed § 126, 1, *a*, and filter the solution from the undissolved binoxide of tin. The filtrate contains the other metals as nitrates. (In presence of bismuth, wash first with water containing nitric acid.) As binoxide of tin is liable to retain traces of copper, the safest way, in an accurate analysis, is to test it for this admixture, and to determine the amount of it as directed in § 143, β.

Brunner ("Journ. f. prakt. Chem.," 58, 446) recommends the following course of proceeding, by which the presence of copper in the tin may be effectively guarded against. Dissolve the alloy in a mixture of 1 part of nitric acid, 4 parts of hydrochloric acid, and 5 parts of water; dilute the solution largely with water, and heat gently. Add crystals of carbonate of soda until a distinct precipitate has formed, and boil. (In presence of copper, the precipitate must, in this operation, change from its original bluish-green to a brown or black tint.) When the fluid has been in ebullition some 10—15 minutes, allow it to cool, and then add nitric acid, drop by drop, until the reaction is distinctly acid, and the precipitate has, after several hours' digestion, acquired a pure white color. The binoxide of tin thus obtained is free from copper; but it may contain some iron, which can be removed as directed in **143** *β*.

Before the binoxide of tin can be considered pure, it must be tested also for silicic acid, as it frequently retains traces of this substance. To this end, it is fused with 3—4 parts of carbonate of soda and potassa, the fused mass boiled with water, and the solution filtered; hydrochloric acid is then added to the filtrate, and, should silicic acid separate, the fluid is filtered off from this substance. The tin is then precipitated by sulphuretted hydrogen, and the silicic acid still remaining in the filtrate is determined in the usual way (§ 140). If hydrochloric acid has produced a precipitate of silicic acid, the last filtration is effected on the same filter (*Khittel*, "Chem. Centralbl.," 1857, 929).

b. TIN FROM THE OXIDES OF GROUPS I., II., III., AS WELL AS FROM PROTOXIDE OF MANGANESE, OXIDE OF ZINC, PROTOXIDE OF NICKEL, PROTOXIDE OF COBALT, OXIDE OF COPPER, and probably also from some other oxides (*Löwenthal*, "Journ. f. prakt. Chem.," 60, 257). **149**

Precipitate the hydrochloric acid solution, which must contain the tin entirely as binoxide (bichloride), as directed § 126, 1, *b*; and separate the precipitated binoxide of tin from the fluid; the filtrate contains the other oxides. In the process, attend to the following points:—

α. Sulphate of soda is generally to be preferred as precipitating agent, where the choice is permitted.

β. When the precipitate of binoxide of tin has subsided, decant the supernatant fluid on to a filter, repeat this operation several times, and then treat the precipitate with a boiling mixture of 1 part of nitric acid of 1·2 sp. gr. and 9 parts of water, before transferring it to the filter for the purpose of completing the washing. The results are very satisfactory.

If the binoxide of tin is mixed with other oxides admitting of reduction by ignition in a current of hydrogen, these oxides may also be reduced in this manner, and the metals then treated as in **148**.

c. ANTIMONY FROM THE METALS OF GROUPS IV. AND V. IN ALLOYS.

Proceed as in **148**, filter the fluid off from the precipitate, and convert the latter into antimonious acid by ignition (§ 125, 2). The results are only approximate, as some teroxide of antimony dissolves. **150**

5. *Methods based upon the Volatility of many Chlorides or Metals.*

a. TIN, ANTIMONY, ARSENIC FROM COPPER, SILVER, LEAD, COBALT, NICKEL.

Treat the sulphides of the metals in a stream of chlorine, proceeding exactly as directed in **132**. In presence of antimony, fill the flasks *f* and *h* (Fig. 80) with a solution of tartaric acid in water, **151** mixed with hydrochloric acid. In alloys also, the metals may be separated by this method. The alloy must be very finely divided. Arsenical alloys are only very slowly decomposed in this way.

b. BINOXIDE OF TIN, TEROXIDE OF ANTIMONY (AND ALSO ANTIMONIC, ARSENIOUS, AND ARSENIC ACIDS), FROM ALKALIES AND ALKALINE EARTHS.

Mix the solid compound with 5 parts of pure chloride of ammonium in powder, in a porcelain crucible, cover this with a concave platinum lid, on which some chloride of ammonium is sprinkled, and ignite gently until all chloride of ammonium is driven off; add a fresh portion of that salt to the contents of the crucible, and repeat the operation until the weight of the latter remains constant. In this process, the chlorides of tin, antimony, and arsenic, escape, leaving the chlorides of the alkalies and alkaline earths. The decomposition by this method proceeds most rapidly with arsenical compounds, less quickly with antimonial compounds, and least so with compounds of tin (*H. Rose*). 152

c. MERCURY FROM GOLD (in alloys and also in other forms of combination).

The two metals are separated by ignition, and the mercury is either calculated from the loss or collected and weighed (§ 118). 153

6. *Methods based upon the Volatility of Tersulphide of Arsenic.*

THE ACIDS OF ARSENIC FROM SESQUIOXIDE OF IRON (probably also from protoxide of nickel, oxide of zinc, oxide of copper, oxide of lead, &c.) *Ebelmen.* 154

Heat the oxides in sulphuretted hydrogen, by which process they are completely converted into sulphides. The tersulphide of arsenic volatilizes, leaving the sulphides of the other metals behind.

7. *Methods based upon the Conversion of Arsenic and Antimony into Arsenates and Antimonates of the Alkalies.*

ARSENIC FROM THE METALS AND OXIDES OF GROUPS II., IV., AND V.

a. If the substance contains the arsenic in the form of arsenites or arsenates, it is fused with 3 parts of carbonate of soda and potassa and 1 part of nitrate of potassa; if an alloy, it is fused with 3 parts of carbonate of soda and 1 part of nitrate of potassa. In either case the residue is boiled with water, and the solution, which contains the arsenates of the alkalies, filtered from the undissolved oxides or carbonates. The arsenic acid is determined in the filtrate as directed § 127, 2. If the quantity of arsenic is only small, the fusion may be effected in a platinum crucible; but if more considerable, the process must be conducted in a porcelain crucible, as platinum would be injuriously affected by it. In the latter case, bear in mind that the fused mass is contaminated with silicic acid and alumina. 155

b. ARSENIC AND ANTIMONY FROM COPPER AND IRON, especially in ores containing sulphur.

Diffuse the very finely pulverized mineral through pure solution of potassa, and conduct chlorine into the fluid (comp. § 148, II., 2, *b*). 156

The iron and copper separate as oxides, the solution contains sulphate, arsenate, and antimonate of potassa (*Rivot*, *Beudant*, and *Daguin*, "Compt. rend.," 1853, 835; "Journ. f. prakt. Chem.," 61, 133).

c. ARSENIC AND ANTIMONY FROM COBALT AND NICKEL.

Dilute the nitric acid solution with water, add a large excess of potassa, heat gently, and conduct chlorine into the fluid until the precipitate is black. The solution contains the whole of the arsenic and antimony, the precipitate the nickel and cobalt, in form of sesquioxide (*Rivot*, *Beudant* and *Daguin*, "Compt. rend.," 1853, 835; "Journ. f. prakt. Chem.," 61, 133). 157

8. *Method based upon the Separation of Arsenic as Arsenate of Suboxide of Mercury.*

ARSENIC ACID FROM THE ALKALIES, ALKALINE EARTHS, OXIDE OF ZINC, PROTOXIDE OF COBALT, PROTOXIDE OF NICKEL, OXIDE OF LEAD, OXIDE OF COPPER, OXIDE OF CADMIUM.

Proceed exactly as in the separation of phosphoric acid by mercury (§ 134, *b*, γ). The arsenic acid *cannot* be determined in the insoluble residue in the way in which the phosphoric acid is determined. Treat the filtrate as directed § 135, 1 (*H. Rose*). 158

9. *Method based upon the Separation of Arsenic as Arsenate of Magnesia and Ammonia.*

ARSENIC ACID FROM ALUMINA AND THE OXIDES OF GROUP IV.

Proceed as directed § 135, *f*, *a*. Treat the precipitated arsenate of magnesia and ammonia the same way as the precipitated phosphate of magnesia and ammonia (see § 135, *f*, *a*). 159

10. *Method based upon the Separation of Arsenic as Arsenio-Molybdate of Ammonia.*

ARSENIC ACID FROM ALL OXIDES OF GROUPS I.—V.

Separate the arsenic acid as directed in § 127, 2 *b*, and treat the filtrate as directed in § 135, *m*. 160

11. *Method based upon the Insolubility of Arsenate of Sesquioxide of Iron.*

ARSENIC ACID FROM THE BASES OF GROUPS I. AND II., AND FROM OXIDE OF ZINC, AND THE PROTOXIDES OF MANGANESE, NICKEL, AND COBALT.

Precipitate the arsenic acid, according to circumstances, as directed § 127, 3, *a* or *b*, filter, and determine the bases in the filtrate. 161

12. *Method based upon the Insolubility of Chloride of Silver.*

SILVER FROM GOLD.

Treat the alloy with cold dilute nitrohydrochloric acid, dilute, and filter the solution of the terchloride of gold from the undissolved chloride of silver. This method is applicable only if the alloy contains less than 15 per cent. of silver; for if it contains a larger proportion, the chloride of silver which forms protects the undecomposed part from the action of the acid. In the same way silver may be separated also from *platinum*. 162

13. *Method based upon the Insolubility of certain Sulphates in Water or Spirit of Wine.*

ARSENIC ACID FROM BARYTA, STRONTIA, LIME, AND OXIDE OF LEAD.

Proceed as for the separation of phosphoric acid from the same oxides (§ 135, *c*). The compounds of these bases with arsenious acid are first converted into arsenates, before the sulphuric acid is added; this conversion is effected by heating the hydrochloric acid solution with chlorate of potassa. **163**

14. *Method based upon the Separation of Copper as Subiodide.*

COPPER FROM ARSENIC AND ANTIMONY.

Dissolve in nitric or sulphuric acid, taking care to add the acid only slightly in excess, dilute with water or, in presence of antimony, with water containing tartaric acid, and precipitate the copper as in **113**. Arsenic and antimony remain in solution (*Flajolot*). **164**

15. *Method based upon the Separation of Copper as Oxalate.*

COPPER FROM ARSENIC.

Add to the nitric acid solution ammonia until the blue precipitate formed remains undissolved upon further addition of the reagent, then effect solution by an excess of oxalate of ammonia. Add, cautiously, hydrochloric or nitric acid to acid reaction, and allow the mixture to stand. The copper separates almost completely as oxalate, which is then converted by ignition in the air into oxide. Add ammonia to the filtrate, and precipitate with a few drops of sulphide of ammonium the minute trace of copper still retained in solution (*F. Field*, "Chem. Gaz.," 1857, 313). **165**

16. *Method based upon the different deportment of the several Metals with Cyanide of Potassium.*

GOLD FROM LEAD AND BISMUTH.

These metals may be separated in solution by cyanide of potassium in the same way in which the separation of mercury from lead and bismuth is effected (see **123**). The solution of the double cyanide of gold and potassium is decomposed by boiling with hydrochloric acid, and, after expulsion of the hydrocyanic acid, the gold determined by one of the methods given in § 123. **166**

II. SEPARATION OF THE OXIDES OF THE SIXTH GROUP FROM EACH OTHER.

§ 165.

Index: *Platinum* from gold, 167;—from antimony, tin, and arsenic, 168.

Gold from platinum, 167;—from antimony, tin, and arsenic, 168.

Tin from gold and platinum, 168;—from arsenic, 169, 176, 177, 178;—from antimony, 171, 175, 177;—protoxide from binoxide of tin, 181.

Antimony from gold and platinum, 168;—from arsenic, 170, 171, 172, 173;—from tin, 171, 175, 177;—teroxide of antimony from antimonic acid, 180, 182.

Arsenic from gold and platinum, 168;—from tin, 169, 176, 177, 178;—from antimony, 170, 171, 172, 173;—arsenious acid from arsenic acid, 174, 179, 182.

1. *Method based upon the Precipitation of Platinum as Potassio-bichloride of Platinum.*

PLATINUM FROM GOLD.

Precipitate from the solution of the chlorides of the metals the platinum as directed § 124, *b*, and determine the gold in the filtrate as directed § 123, *b*. 167

2. *Method based upon the Volatility of the Chlorides of the inferior Metals.*

PLATINUM AND GOLD FROM TIN, ANTIMONY, AND ARSENIC.

Heat the finely divided alloy or the sulphides in a stream of chlorine gas. Gold and platinum are left, the chlorides of the other metals volatilize (compare **132**, **133**). 168

3. *Methods based upon the Volatility of Arsenic and Tersulphide of Arsenic.*

a. ARSENIC FROM TIN (*H. Rose*).

Convert into sulphides or into oxides, dry at 212° F., and heat a weighed portion of the dried mass in a bulb-tube, gently at first, but gradually more strongly, conducting a stream of dry sulphuretted hydrogen gas through the tube during the operation. Sulphur and tersulphide of arsenic volatilize, sulphide of tin is left. The tersulphide of arsenic is received in a small flask connected with the bulb-tube, in the manner described in **132**, which contains dilute solution of ammonia. When upon continued application of heat no further sign of sublimation is observed in the colder part of the tube, drive off the sublimate which has collected in the bulb, allow the tube to cool, and then cut it off above the coating. Divide the separated portion of the tube into pieces, and heat these with solution of soda until the sublimate is dissolved; unite the solution with the ammoniacal fluid in the receiver, add hydrochloric acid, then, without filtering, chlorate of potassa, and heat gently until the tersulphide of arsenic is completely dissolved. Filter from the sulphur, and determine the arsenic acid as directed § 127, 2. The quantity of tin cannot be calculated at once from the blackish-brown sulphide of tin in the bulb, since this contains more sulphur than corresponds to the formula Sn S. It is therefore weighed, and the tin determined in a weighed portion of it, by converting it into binoxide, which is effected by moistening with nitric acid, and ignition (§ 126, 1, *c*). 169

Tin and arsenic in alloys are more conveniently converted into oxides by cautious treatment with nitric acid. If, however, it is wished to convert them into sulphides, this may readily be effected by heating 1 part of the finely divided alloy with 5 parts of carbonate of soda, and 5 parts of sulphur, in a covered porcelain crucible, until the mass is in a state of calm fusion. It is then allowed to cool, dissolved in water, the solution filtered from the sulphide of iron, &c., which may possibly have formed, and the filtrate precipitated with hydrochloric acid.

b. ARSENIC FROM ANTIMONY IN ALLOYS.

170 Heat a weighed portion of the finely divided alloy with 2 parts of carbonate of soda and 2 parts of cyanide of potassium in a bulb-tube, through which dry carbonic acid is transmitted; apply a gentle heat at first, but increase this gradually to a high degree of intensity, and continue heating until no more arsenic volatilizes. Take care not to inhale the escaping fumes; the safest way is to insert the hind part of the bulb-tube into a flask, in which the arsenic will sublime. Allow the bulb-tube to cool; after cooling, treat the contents, first with a mixture of equal parts of spirit of wine and water, then with water, and weigh the residuary antimony. The quantity of the arsenic is calculated from the loss. This method gives only approximate results. The direct fusion of the alloy in a stream of carbonic acid or hydrogen gas, without previous addition of carbonate of soda and cyanide of potassium, would give most inaccurate results, as a large quantity of antimony volatilizes under these circumstances.

4. *Methods based upon the insolubility of Antimonate of Soda.*

a. ANTIMONY FROM TIN AND ARSENIC (*H. Rose*).

171 Oxidize a weighed sample of the finely divided substance, in a porcelain crucible, with nitric acid of 1·4 specific gravity, adding the acid gradually. Dry the mass on the water-bath, transfer to a silver crucible, rinsing the last particles adhering to the porcelain into the silver crucible with solution of soda, dry again, add eight times the bulk of the mass of solid hydrate of soda, and fuse for some time. Allow the mass to cool, and then treat with hot water until the undissolved residue presents the appearance of a fine powder; dilute with some water, and add alcohol of 0·83 sp. gr. in sufficient quantity to make the proportion of its volume to that of the water as 1 to 3. Allow the mixture to stand for 24 hours, with frequent stirring; then filter, transfer the last adhering particles from the crucible to the filter by rinsing with dilute spirit of wine (1 volume of alcohol to 3 volumes of water), and wash the undissolved residue on the filter, first with spirit of wine containing 1 volume of alcohol to 2 volumes of water, then with a mixture of equal volumes of alcohol and water, and finally with a mixture of 3 volumes of alcohol and 1 of water. Add to each of the alcoholic fluids used for washing a few drops of solution of carbonate of soda. Continue the washing until the color of a portion of the fluid running off remains unaltered upon being acidified with hydrochloric acid and mixed with sulphuretted hydrogen water.

Rinse the antimonate of soda from the filter, wash the latter with a mixture of hydrochloric acid and tartaric acid, dissolve the antimonate in this mixture, precipitate with sulphuretted hydrogen, and determine the antimony as directed § 125, 1.

To the filtrate, which contains the tin and arsenic, add hydrochloric acid, which produces a precipitate of arsenate of binoxide of tin; conduct now into the unfiltered fluid sulphuretted hydrogen for some time, allow the mixture to stand at rest until the odor of that gas has almost completely gone off, and then separate the weighed sulphides of the metals as in 169.

If the substance contains only *antimony* and *arsenic*, the alcoholic filtrate is heated, with repeated addition of water, until the fluid scarcely retains the odor of alcohol; hydrochloric acid is then added, and the arsenic determined as arsenate of magnesia and ammonia (§ 127, 2).

b. DETERMINATION OF THE SULPHIDE OF ARSENIC CONTAINED IN THE COMMERCIAL SULPHIDE OF ANTIMONY (*Wackenroder*).

Deflagrate 20 grammes of the finely pulverized sulphide of antimony with 40 grammes of nitrate of potassa and 20 grammes of carbonate of soda, by projecting the mixture gradually into a red-hot hessian crucible; treat the strongly ignited mass repeatedly with water, filter the solution, acidify the filtrate with hydrochloric acid, treat with sulphurous acid, and precipitate the arsenic with sulphuretted hydrogen. Digest the moist precipitate, which contains a small admixture of antimony, with carbonate of ammonia, filter, acidify the filtrate, conduct sulphuretted hydrogen into the fluid, and determine the arsenic as tersulphide as directed § 127, 4. 172

5. *Methods based upon the Precipitation of Arsenic as Arsenate of Magnesia and Ammonia.*

a. ARSENIC FROM ANTIMONY.

Oxidize the metals or sulphides with nitrohydrochloric acid or hydrochloric acid and chlorate of potassa, or with chlorine in alkaline solution (see § 148, II., 2, *b*); add tartaric acid, a large quantity of chloride of ammonium, and then ammonia in excess. Should the addition of the latter reagent produce a precipitate, this is a proof that an insufficient quantity of chloride of ammonium or of tartaric acid has been used, which error must be corrected before proceeding with the analysis. Then precipitate the arsenic acid as directed § 127, 2, and determine the antimony in the filtrate as directed § 125, 1. As basic tartrate of magnesia might precipitate with the arsenate of magnesia and ammonia, the precipitate should always, after slight washing, be redissolved in hydrochloric acid, and the solution precipitated again with ammonia. 173

b. ARSENIOUS ACID FROM ARSENIC ACID.

Mix the solution with a large quantity of chloride of ammonium, precipitate the arsenic acid as directed § 127, 2, and determine the arsenious acid in the filtrate by precipitation with sulphuretted hydrogen (§ 127, 4). 174

6. *Methods based upon the Precipitation of the Metals in the metallic state.*

a. TIN FROM ANTIMONY (*Gay-Lussac*).

Heat a weighed portion of the finely divided alloy (or other form of combination) with hydrochloric acid, add chlorate of potassa in small portions until the mass is dissolved, and then divide the fluid into two equal parts, *a* and *b*. In *a* precipitate both metals on a tin rod, rinse them off, and weigh; add to *b* a tolerably large 175 amount of hydrochloric acid, introduce a clean slip of tin, and heat for some time. By this process, the antimony is completely thrown down in form of a black powder, and the bichloride of tin reduced to protochloride. Wash the antimony off the tin with water containing hydrochloric acid, collect upon a weighed filter, dry, and weigh. The difference gives the quantity of tin.

b. DETERMINATION OF ARSENIC IN METALLIC TIN (*Gay-Lussac.* "Ann. de Chim. et de Phys.," 23, 228; *Liebig* and *Kopp's* "Annual Report," 1847 and 1848, page 968).

Dissolve the laminated or granulated* metal in a mixture of 1 equivalent of nitric acid and 9 equivalents of hydrochloric acid, with the aid of a gentle heat. The solution ensues without evolution of gas; protochloride of tin and chloride of ammonium are formed, the arsenic is left in the form of powder. $NO_5 + 9\ HCl + 8\ Sn = 8\ SnCl + NH_4\ Cl + 5HO$. The nitro-hydrochloric acid must, therefore, not be used in a much larger proportion than will give to 8 equivalents of metal 1 equivalent of NO_5, and 9 equivalents of HCl. **176**

7. *Method based upon the Precipitation of some of the Metals as Sulphides by Hyposulphite of Soda.*

ARSENIC AND ANTIMONY FROM TIN.

Mix the solution with hydrochloric acid in excess, heat to boiling, and add hyposulphite of soda until the precipitate appears no longer orange or yellow, but white, and the fluid looks opalescent, owing to the separation of sulphur. Arsenic and antimony are completely precipitated, whilst the whole of the tin remains in solution (*Vohl*, "Annal. d. Chem. u. Pharm.," 96, 240). If arsenic alone is present in the precipitate, determine the metal as directed § 127, 4; if antimony alone, as directed § 125, 1; if both metals are present, separate them according to the instructions of **171** or **173**. The tin in the filtrate is estimated best as directed § 126, *c.* **177**

8. *Method based upon the Precipitation of Tin as Arsenate of Binoxide of Tin.*

TIN FROM ARSENIC.

Ed. Häffely ("Phil. Mag.," x. 220) has proposed the following method of determining both the tin and the arsenic in commercial stannate of soda, which often contains a large admixture of arsenate of soda. Mix a weighed sample with a known quantity of arsenate of soda in excess, add nitric acid also in excess, boil, filter the precipitate, which has the composition $2\ SnO_2, AsO_5 + 10\ Aq$, and wash; expel the water by ignition, and weigh the residue, which consists of $2\ SnO_2, AsO_5$. In the filtrate determine the excess of arsenic acid as directed § 127, 2 or 4. Calculate the amount of binoxide of tin from the weight of the ignited residue; and that of the arsenic acid from the weight of the latter, joined to the quantity found in the filtrate, after deducting the amount added. **178**

9. *Volumetrical Methods.*

a. ARSENIOUS FROM ARSENIC ACID.

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* Prepared by pouring the fused metal into water.

Convert the whole of the arsenic in a portion of the substance 179
into arsenic acid and determine the total amount of this as directed § 127, 2; determine in another portion the arsenious acid as directed § 127, 5, *a* or *b*, and calculate the arsenic acid from the difference.

b. TEROXIDE OF ANTIMONY FROM ANTIMONIC ACID.

Determine in a sample of the substance the total amount of the 180
antimony as directed § 125, 1, in another portion that of the teroxide as directed § 125, 3, and calculate the antimonic acid from the difference.

10. *Methods based upon the Indirect Gravimetric Determination of one of the Oxides.*

a. PROTOXIDE OF TIN IN PRESENCE OF BINOXIDE.

Determine in a portion of the substance the total quantity of the 181
tin; dissolve another portion in hydrochloric acid, taking care to exclude the air, and drop the solution into a large excess of solution of chloride of mercury, with stirring. Treat the precipitated subchloride of mercury as directed § 117, 1. One equivalent (Hg_2Cl) corresponds to 1 equivalent of protochloride of tin ($SnCl$) (*H. Rose*).

b. ARSENIOUS ACID IN PRESENCE OF ARSENIC ACID;—TEROXIDE OF ANTIMONY IN PRESENCE OF ANTIMONIC ACID.

Determine in a portion of the substance the total quantity of the 182
arsenic; dissolve another portion in hydrochloric acid (of course, no oxidizing agents, such as nitrates, &c., must be present), and add an excess of solution of sodio- or ammonio-terchloride of gold. Let the mixture stand several days (properly protected from dust), in the cold, or, in the case of dilute solutions, at a gentle heat; filter the fluid from the separated gold, and determine the latter as directed § 123, *b*. Keep the filtrate to see whether an additional quantity of gold may not separate, which is sometimes the case. 2 equivalents of gold correspond to 3 equivalents of arsenious acid ($2\,AuCl_3 + 3\,AsCl_3 = 3\,AsCl_5 + 2\,Au$). The same method may be employed also to determine teroxide of antimony in presence of antimonic acid; however, in the case of antimony, a larger excess of hydrochloric acid must be added, to effectively prevent the precipitation of antimonic acid. The gold should be washed with water containing hydrochloric acid (*H. Rose*).

II. THE SEPARATION OF THE ACIDS FROM EACH OTHER.

I have again to remark that the methods of separation given in the following paragraphs proceed generally upon the assumption that the acids exist either in the free state, or in combination with alkaline bases. Compare the introductory remarks on the subject, § 151. Where several acids are present in one and the same substance, the analysis is often effected by determining one acid in one portion, the other in another portion. Of course, the methods here given do not embrace every imaginable case, but only the most important cases, and those of most frequent occurrence.

FIRST GROUP.

ARSENIOUS ACID—ARSENIC ACID—CHROMIC ACID—SULPHURIC ACID—PHOSPHORIC ACID—BORACIC ACID—OXALIC ACID—HYDROFLUORIC ACID—SILICIC ACID—CARBONIC ACID.

§ 166.

1. Arsenious Acid and Arsenic Acid from all other Acids.

Precipitate the arsenic from the solution by means of sulphuretted hydrogen (§ 127, 4), filter, and determine the other acids in the filtrate. If chromic acid is present, this is reduced, before the addition of the sulphuretted hydrogen, by one of the methods given in § 130; as sulphur would fall down with the tersulphide of arsenic if this precaution were neglected. 183

If arsenic acid is present the fluid is heated to 158° F., which greatly facilitates its precipitation; or the acid is reduced to arsenious acid, by means of sulphurous acid, before adding the sulphuretted hydrogen. From those acids which form soluble salts with magnesia, arsenic acid may be separated also by precipitation as arsenate of magnesia and ammonia as directed § 127, 2.

2. Sulphuric Acid from the other Acids.

a. From the Acids of Arsenic, from Phosphoric, Boracic, Hydrofluoric, Oxalic, Silicic, and Carbonic Acids.

Acidify the dilute solution strongly with hydrochloric acid, mix with chloride of barium, and filter the sulphate of baryta from the solution, which contains all the other acids. Determine the sulphate of baryta as directed § 132. 184

b. From Hydrofluoric Acid in Insoluble Compounds.

A mixture of sulphate of baryta and fluoride of calcium cannot be decomposed by simple treatment with hydrochloric acid; the insoluble residue always contains, besides sulphate of baryta, sulphate of lime and fluoride of barium. The object in view may be attained, however, by the following process:—Fuse the substance with 6 parts of carbonate of soda and potassa, and 2 parts of silicic acid; allow the mass to cool, treat with water, and add carbonate of ammonia to the solution obtained; filter, wash the separated silicic acid with dilute solution of carbonate of ammonia, supersaturate the filtrate with hydrochloric acid, and precipitate with chloride of barium. 185

If you wish to determine the fluorine also, acidify with nitric acid, precipitate with nitrate of baryta, then saturate with carbonate of soda, and precipitate the fluoride of barium by spirit of wine. Wash a long time, first with spirit of wine of 50 per cent., then with strong alcohol; dry, ignite, and weigh. The insoluble residue left upon treating with water contains the baryta and lime. Dissolve in hydrochloric acid, filter from the undissolved silicic acid, and determine the bases in the filtrate as directed § 154 (*H. Rose*).

c. In Presence of a large proportion of Chromic Acid.

Reduce the chromic acid by boiling the dry compound with concentrated hydrochloric acid (if this process is conducted accord- 186 ing to the directions of § 130, I., *d*, *β*, it gives, at the same time, the quantity of the chromic acid); dilute the solution largely, and precipitate, first the sulphuric acid by adding a small excess of chloride of barium, then the excess of baryta by sulphuric acid, and lastly the sesquioxide of chromium by ammonia.

d. From Hydrofluosilicic Acid.

Precipitate the hydrofluosilicic acid as directed § 133, then the sulphuric acid in the filtrate by baryta. 187

3. Phosphoric Acid from the other Acids.

a. From the *acids of arsenic*, see **183**; from *sulphuric acid*, see **184**.

b. From Chromic Acid.

Precipitate the phosphoric acid as phosphate of magnesia and ammonia (§ 134, *b*). Determine the chromic acid in the filtrate as directed § 130, *a*, *β*, *b*, *c*, or *d*. 188

c. From Boracic Acid.

Precipitate the phosphoric acid as in **188**, and determine the boracic acid in the filtrate as directed § 136, II., *b*. 189

d. From Oxalic Acid.

α. If the two acids are to be determined in one and the same sample of the substance, the aqueous solution is mixed with sodio-terchloride of gold in excess, heat applied, and the quantity of oxalic acid present calculated from that of the reduced gold (§ 137, *c*, *α*). The gold added in excess is separated from the filtrate by means of sulphuretted hydrogen, and the phosphoric acid then precipitated by sulphate of magnesia. If the compound is insoluble in water, hydrochloric acid is used as solvent, and the process conducted as directed § 137, *c*, *β*. 190

β. If there is a sufficient quantity of disposable substance, the oxalic acid is determined in one portion according to the directions of § 137, *b*, or *d*, and the phosphoric acid in another portion. If the substance is soluble in water, and the quantity of oxalic acid inconsiderable, the phosphoric acid may be precipitated at once with sulphate of magnesia, chloride of ammonium, and ammonia: if not, the substance is ignited with carbonate of soda and potassa, which destroys the oxalic acid, and the phosphoric acid is determined in the residue. 191

e. Phosphates from Fluorides.

α. The substance is soluble in water.

aa. If the substance contains a *relatively large* quantity of fluorine, which will permit the estimation of the latter from the difference, precipitate the solution by chloride of calcium, wash, dry, ignite, and weigh. The residue consists of phosphate of lime and fluoride of calcium. Heat in a platinum vessel, with sulphuric acid, until all the fluorine has escaped as hydrofluoric acid, taking care not to raise the heat to a degree at which sulphuric acid volatilizes; then determine the lime and the phosphoric acid as directed § 135, *c*. By de- 192 ducting the phosphoric acid and lime from the total weight of the precipitate, the fluorine is found by the following calculation :—

The eq. of the fluorine less the eq. of the oxygen : the eq. of the fluorine
: :
the ascertained loss of weight : the fluorine sought.

bb. If the substance contains a *relatively small* proportion of fluorine, mix the solution with basic nitrate of suboxide of mercury. A yellow precipitate of basic phosphate of suboxide of mercury is produced, the fluoride of mercury remaining in solution. Determine the phosphoric acid in the precipitate as directed § 134, *b*, γ. Neutralize the filtrate with carbonate of soda, conduct sulphuretted hydrogen into the unfiltered fluid, then filter, and determine the fluorine as directed § 138, I. (*H. Rose*). 193

β. *The substance is not soluble in water, but decomposed by acids* (*e. g.*, Apatite, Bone-ash).

Dissolve in hydrochloric acid, evaporate with sulphuric acid, as in **192**, until the fluorine is completely expelled, and determine in the residue the phosphoric acid on the one part, the oxides on the other. Now, if you know the proportion between the phosphoric acid and the bases in the analysed compound, you may readily calculate the expelled fluorine by the excess of the bases, the oxygen of the latter being equivalent to the fluorine. 194

γ. *The substance is insoluble in water and not decomposed by acids.*

Fuse with carbonate of soda and silicic acid as in **185**, treat the fused mass with water, and the solution with carbonate of ammonia. You have now in solution the whole of the fluorine and phosphoric acid in combination with an alkali (*H. Rose*), and may accordingly proceed as in **192** or **193**. 195

4. Fluorides from Borates.

Mix the solution assumed to contain borate and fluoride of an alkali metal with some carbonate of soda, and add chloride of calcium in excess. A precipitate is formed, which contains the whole of the fluorine or fluoride of calcium, and besides this, carbonate and some borate of lime; the greater proportion of the latter having been redissolved by the excess of the lime salt added. Determine the fluoride of calcium in the precipitate as directed in § 138, I. The small quantity of boracic acid in the precipitate is, in this process, partly volatilized, partly dissolved, after evaporating he mass with acetic acid and extracting with water. It is therefore necessary to determine the boracic acid in a separate portion of the substance; this is effected according to the directions of § 136, 2 (*A. Stromeyer*, "Journ. f. prakt. Chem.," 100, 91). 196

5. Fluorides from Silicic Acid and Silicates.

A great many native silicates contain fluorides; care must, therefore, always be taken, in the analysis of minerals, not to overlook the latter.

If the silicates containing fluoride are decomposable by acids (which is only rarely the case)—and the silicic acid is separated, in the usual way, by evaporation, the whole of the fluorine may volatilize.

α. *Berzelius's* method.

Fuse the elutriated substance with 4 parts of carbonate of soda, for some time, at a strong red heat; digest the mass in water, boil, filter, and wash, first with boiling water, then with solution of carbonate of ammonia. The filtrate contains all the fluorine as fluoride of sodium, and, besides this, carbonate of soda, silicate of soda, and aluminate of soda. Mix the filtrate with carbonate of ammonia and heat the mixture, replacing the carbonate of ammonia which evaporates. Filter off the precipitate of hydrate of silicic acid and hydrate of alumina, and wash with carbonate of ammonia. Heat the filtrate until the carbonate of ammonia is completely expelled, and determine the fluorine as directed § 138. To separate the silicic acid, decompose the two precipitates with hydrochloric acid as directed § 140, II., *a.** 197

β. *Wöhler's* method (suitable only for the analysis of substances which contain a large proportion of fluorine and are readily decomposed by sulphuric acid). 198

Reduce the compound under examination to the very finest powder, introduce this into a small flask, pour pure sulphuric acid over it, close the flask quickly with a perforated cork into which a small tube with chloride of calcium is fitted, weigh the apparatus with the greatest despatch, and then apply heat until the evolution of fumes of fluoride of silicon ($Si\ Fl_3$) ceases; remove the last remaining traces of the gas from the flask, by an exhausting syringe, let the apparatus cool, and then weigh. The loss indicates the weight of the fluoride of silicon expelled in the process. Deduce from this the quantity both of the fluorine and of the silicon, calculate the latter as silicic acid, and add the quantity found to the weight of the silicic acid in the residue.

6. FLUORIDES, SILICATES, AND PHOSPHATES, IN PRESENCE OF EACH OTHER.

Native compounds of fluorides, silicates, and phosphates are not uncommon. They are decomposed as in 197. Complete decomposition of the phosphates is not always effected in this process, as phosphate of lime, for instance, is only partially decomposed by fusion with carbonate of soda. The solution remaining after the separation and removal of the silicic acid and the volatilization of the carbonate of ammonia, contains—in presence of phosphates—besides fluoride of sodium and carbonate of soda, also phosphate of soda. 199

Neutralize the fluid nearly with hydrochloric acid, precipitate with chloride of calcium, filter, dry, and ignite the precipitate, which consists of fluoride of calcium, phosphate of lime, and carbonate of lime; treat the residue with acetic acid in excess, and evaporate on the water-bath to dryness and complete expulsion of the acetic acid; treat the acetate of lime, into which the carbonate has been converted by the last operation, with water, weigh the residue, which consists of phosphate of lime and fluoride of calcium, and effect its ulterior decomposition as directed in **192**. In the original residue of the first operation and in the precipitate thrown down by carbonate of ammonia, determine the silicic acid, the rest of the phosphoric acid, and the bases.

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* The whole of the silicic acid may be removed from the filtrate by treating with carbonate of ammonia: addition of carbonate of zinc and ammonia, as recommended by *Berzelius*, and afterwards by *Regnault*, appears therefore superfluous (*H. Rose*).

7. SILICIC ACID FROM ALL OTHER ACIDS.

a. In Compounds which are decomposed by Hydrochloric Acid.

Decompose the substance by digestion with hydrochloric acid or nitric acid, evaporate on the water-bath* to dryness (§ 140, II., *a.*), and treat the residue, according to circumstances, with water, hydrochloric acid, or nitric acid; filter the fluid from the residuary silicic acid, and determine the other acids in the filtrate. In presence of boracic acid, or fluorine, this method is inapplicable, and the process described in *b* (**201**) is employed instead. If carbonates are present, the carbonic acid is determined in a separate portion of the substance. **200**

b. In Compounds which are not decomposed by Hydrochloric Acid.

Decompose the substance by ignition with carbonate of soda and potassa (§ 140, II., *b*, *a.*), and either treat the residue at once cautiously with dilute hydrochloric or nitric acid, and the solution thus obtained as in *a* (**200**); or treat the residue with water, precipitate the silicic acid from the solution by heating with bicarbonate of ammonia, filter, add the precipitate to the undissolved residue, and determine the silicic acid, in the united mass, by treating with hydrochloric acid, and proceeding as directed § 140, II., *a.* Determine the other acids in the filtrate. Which of these two methods may be preferable in particular cases, depends upon the nature of the bases, and upon the relative proportion which the silicic acid bears to the latter. In presence of boracic acid and fluorine, the latter method alone is applicable. **201**

8. CARBONIC ACID FROM ALL OTHER ACIDS.

When carbonates are heated with stronger acids, the carbonic acid is expelled; the presence of carbonates, therefore, does not interfere with the quantitative estimation of most other acids. And as, on the other hand, the carbonic acid is determined by the loss of weight or by combination of the expelled acid, the presence of salts of non-volatile acids does not interfere with the determination of the carbonic acid. Accordingly, compounds containing carbonates, sulphates, phosphates, &c., are analysed in two separate portions, the carbonic acid being determined in one, the other acids in the other sample. In presence of fluorides, one of the *weak* non-volatile acids, such as tartaric acid or citric acid, must be employed to expel the carbonic acid; since, were sulphuric acid or hydrochloric acid used for the purpose, part of the liberated hydrofluoric acid would escape with the carbonic acid. The process described in § 139, II., *e*, *β*, may be employed, without modification, in presence of fluorides. If, as will occasionally happen in **202** an analysis, a mixed precipitate of fluoride of calcium and carbonate of lime is thrown down from a solution, the two salts may be separated by evaporating the mixed precipitate with acetic acid to dryness, and treating the residue with water: the acetate of lime formed from the carbonate is dissolved, the fluoride of calcium is left undissolved.

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* A higher temperature would not answer.

SECOND GROUP.

HYDROCHLORIC ACID — HYDROBROMIC ACID — HYDRIODIC ACID— HYDROCYANIC ACID—HYDROSULPHURIC ACID.

I. SEPARATION OF THE ACIDS OF THE SECOND GROUP FROM THOSE OF THE FIRST.

§ 167.

a. Separation of all the Acids of the Second Group from those of the First.

Mix the dilute solution of the compound under examination with nitric acid, add solution of nitrate of silver in excess, and filter the fluid from the insoluble chloride, bromide, iodide, &c., of silver. The filtrate contains the whole of the acids of the first group, the silver salts of these acids being soluble in water or in nitric acid. Carbonic acid must, under all circumstances, be determined in a separate portion. If this is done as directed § 139, II., *e*, in presence of chlorides, hydrochloric acid will escape with the carbonic acid. In accurate analyses this is prevented by adding a solution of sulphate of silver in slight excess, or, according to *Vohl*, by adding some finely levigated oxide of mercury; which addition will also prevent the escape of sulphuretted hydrogen in presence of sulphides; the latter object may be attained also by adding some neutral chromate of potassa. 203

b. Separation of some of the Acids of the Second Group from Acids of the First Group.

As it is often inconvenient for the ulterior separation of the acids of the second group to have them all in the form of insoluble silver compounds, the analysis is sometimes effected by separating first the acid of the first group, then that of the second. If the quantity of disposable substance is large enough, the most convenient way generally is to determine the several acids, *e.g.*, sulphuric acid, phosphoric acid, chlorine, sulphuretted hydrogen, &c., in separate portions. 204

Of the infinite number of combinations that may present themselves we will here consider only the most important.

1. SULPHURIC ACID may be separated from chlorine, bromine, iodine, and cyanogen, by precipitation with a salt of baryta. If the acids of the second group are to be determined in the same portion, nitrate of baryta or acetate of baryta is used instead of chloride of barium. In presence of sulphuretted hydrogen, sulphuric acid cannot be determined in this way, as part of the solution of the sulphuretted hydrogen would be converted into sulphuric acid by the oxygen of the air. The error thus introduced into the process may be very considerable (*Fresenius*, "Journ. f. prakt. Chem.," 205

70, 9). The sulphuretted hydrogen must, therefore, first be removed by addition of chloride of copper, and the sulphuric acid determined in the filtrate; or, the sulphuretted hydrogen must be completely oxidized and converted into sulphuric acid by chlorine, and a corresponding deduction afterwards made in calculating the quantity of the sulphuric acid.

2. PHOSPHORIC ACID may be precipitated by means of nitrate of magnesia and ammonia, after addition of nitrate of ammonia; oxalic acid by nitrate of lime; chlorine, bromine, iodine, &c., are determined in the filtrate. 206

3. CHLORINE IN SILICATES.

a. If the silicates dissolve in dilute nitric acid, precipitate the solution with nitrate of silver, without applying heat, remove the excess of silver from the filtrate by dilute hydrochloric acid, still without applying heat, and then separate the silicic acid in the usual way. 207

b. If the silicate becomes gelatinous upon its decomposition with nitric acid, dilute, allow to deposit, filter, wash the separated silicic acid, and treat the filtrate as in *a*.

c. If nitric acid fails to decompose the silicates, mix the substance with carbonate of soda and potassa, and moisten the mass with water; dry in the crucible, fuse, boil with water, remove the silicic acid which may have dissolved, by means of carbonate of ammonia (185), and then precipitate, after addition of nitric acid, with nitrate of silver (*H. Rose*).

4. CHLORIDES IN PRESENCE OF FLUORIDES.

If the substance is soluble in water, the separation may be effected as directed in 203; but it is more convenient to precipitate the fluorine with nitrate of lime, and the chlorine in the filtrate with solution of nitrate of silver. Insoluble compounds are fused with carbonate of soda and silicic acid (see 185). 208

5. CHLORINE IN PRESENCE OF FLUORINE, IN SILICATES.

Proceed as directed 197. Saturate the alkaline filtrate nearly with nitric acid, precipitate with nitrate of lime, separate the fluoride of calcium and the carbonate of lime as directed in 202, and precipitate the chlorine in the filtrate by solution of nitrate of silver. 209

6. SULPHIDES IN SILICATES.

If the substance is decomposed by acids, reduce it to the very finest powder, and treat with fuming nitric acid (§ 148, II., 2, *a*). When the sulphur is completely oxidized, dilute, filter off the silicic acid, add carbonate of ammonia to the filtrate, to remove the portion of silicic acid which may possibly have dissolved, filter again, and determine in the filtrate the sulphuric acid formed. If the substance is not decomposed by acids, fuse with 4 parts of carbonate of soda and 1 part of nitrate of potassa, boil the fused mass with water, filter, remove the dissolved silicic acid from the filtrate by carbonate of ammonia (185), filter again, and determine in the filtrate the sulphuric acid produced from the sulphur. 210

Supplement.

ANALYSIS OF COMPOUNDS CONTAINING SULPHIDES OF THE ALKALI METALS, CARBONATES, SULPHATES, AND HYPOSULPHITES.

§ 168.

The following method was first employed by *G. Werther* ("Journ. f. prakt. Chem.," *55*, 22), in the examination of gunpowder residues. 211

Put the substance into a flask, pour over it water, in which a sufficient quantity of carbonate of oxide of cadmium* is suspended; insert the cork, and shake the vessel frequently. The sulphide of the alkali metal decomposes completely with the carbonate of cadmium. Filter the yellowish precipitate off, and treat with dilute acetic acid (not with hydrochloric acid); the carbonate of cadmium dissolves, the sulphide of cadmium is left undissolved. Oxidize the latter with chlorate of potassa and nitric acid (§ 148, II., 2, *a*, *β*), and precipitate with chloride of barium the sulphuric acid formed from the sulphide.

Heat the fluid filtered from the yellow precipitate, and mix with solution of neutral nitrate of silver. The precipitate thrown down by that reagent consists of carbonate of silver and sulphide of silver ($K\,O, S_2O_2 + Ag\,O, N\,O_5 = K\,O\,S\,O_3 + Ag\,S + N\,O_5$). Remove the former salt by means of ammonia, and precipitate from the ammoniacal solution the silver—after acidifying with nitric acid—by means of chloride of sodium. Each equivalent of chloride of silver so obtained corresponds to an equivalent of carbonate.† Dissolve the sulphide of silver in dilute boiling nitric acid, determine the silver in the solution as chloride of silver, and calculate from the result the quantity of the hyposulphite; 1 equivalent of $Ag\,Cl$ corresponds to 2 equivalents of sulphur in hyposulphurous acid, and accordingly to 1 equivalent of hyposulphite ($K\,O, S_2O_2$).

From the fluid filtered from the sulphide and carbonate of silver, remove first the excess of silver by means of hydrochloric acid, and then precipitate the sulphuric acid by a salt of baryta. From the weight of the sulphuric acid found you have, of course, to deduct an amount corresponding to the quantity of that acid resulting from the decomposition of the hyposulphurous acid, and accordingly for 1 equivalent of chloride of silver formed from the sulphide, 0·28 eq. of sulphuric acid. The difference gives the amount of sulphuric acid originally present in the analysed compound. By way of control, you may determine, in the fluid filtered off from the sulphate of baryta, the alkali as sulphate as directed in § 97 or § 98.

II. SEPARATION OF THE ACIDS OF THE SECOND GROUP FROM EACH OTHER.

§ 169.

1. CHLORINE FROM BROMINE.

All the methods of direct analysis hitherto proposed to effect the 212 separation of chlorine from bromine are defective. The bromine is therefore usually determined in a more indirect way.

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* To obtain the carbonate of oxide of cadmium free from alkali, carbonate of ammo must be used as precipitant.

† A quantity equivalent to the sulphide found has to be deducted from this ($K\,S + Cd\,O,$ $C\,O_2 = Cd\,S + K\,O, C\,O_2$).

a. Precipitate with nitrate of silver, wash the precipitate, dry, fuse, and weigh. Transfer an aliquot part of the mixed chloride and bromide of silver to the bulb of a weighed bulb-tube,* fuse in the bulb, let the mass cool, and weigh. This operation gives both the total weight of the tube with its contents, and the weight of the portion of mixed chloride and bromide of silver in the bulb. The greatest accuracy in the several weighings is indispensable. Now transmit through the tube a slow stream of dry pure chlorine gas, heat the contents of the bulb to fusion, and shake the fused mass occasionally about in the bulb. After the lapse of about 20 minutes, take off the tube, allow it to cool, hold it in an oblique position, that the chlorine gas may be replaced by atmospheric air, and then weigh. Heat once more, for about 10 minutes, in a stream of chlorine gas, and weigh again. If the two last weighings agree, the experiment is terminated; if not, the operation must be repeated once more. The loss of weight suffered, multiplied by 4·223 gives the quantity of the bromide of silver decomposed by the chlorine. For the mode of calculating the results, see § 200. The mixed chloride and bromide of silver may also be heated in a current of chlorine gas, instead of in a bulb-tube, in a small porcelain-boat inserted into a glass tube.

This method gives very accurate results if the proportion of bromine present is not too small; but most uncertain results in cases where mere traces of bromine have to be determined in presence of large quantities of chlorides, as, for instance, in saline springs. To render the method available in such cases, the great point is to produce a silver compound containing all the bromine, and only a small part of the chlorine. This end may be attained in several ways.

a. *Fehling's* method ("Journ. f. prakt. Chem.," 45, 269).

Mix the solution *cold* with a quantity of solution of nitrate of silver 213
not nearly sufficient to effect complete precipitation, shake the mixture vigorously, and leave the precipitate for some time in the fluid, with repeated shaking. If the amount of the precipitate produced corresponds at all to the quantity of bromine present, the whole of the latter substance is obtained in the precipitate.

Fehling recommends the following proportions :—

To 0·001 of bromine use $\frac{1}{5}$ or $\frac{1}{6}$ the quantity of solution of nitrate of silver that would be required to effect complete precipitation ;—to 0·0001 of bromine, $\frac{1}{10}$;—to 0·00002 of bromine, $\frac{1}{30}$;—to 0·00001 of bromine, $\frac{1}{50}$.

Wash the mixed precipitate of chloride and bromide of silver *thoroughly*, dry, ignite, weigh, and treat with chlorine, as above. To find the quantity of the chlorine, precipitate another weighed portion of the original solution completely with solution of nitrate of silver, and deduct from the weight of the precipitate the quantity of bromide of silver found.

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* The best way of effecting the transfer of this portion from the crucible to the tube is to fuse the mass in the crucible again, and then let a portion of it run from the latter into the tube.

β. Marchand ("Journ. f. prakt. Chem.," 47, 363) has slightly 214 modified *Fehling's* method. He reduces with zinc the mixed precipitate of chloride and bromide of silver obtained by *Fehling's* fractional precipitation, decomposes the solution of chloride and bromide of zinc with carbonate of soda, evaporates to dryness, and treats the residue with absolute alcohol, which dissolves all the bromide of sodium with only a little of the chloride of sodium; he then evaporates the solution to dryness, treats the residue with water, precipitates again with solution of nitrate of silver, and subjects a part of the weighed precipitate to the treatment with chlorine.

γ. If a fluid containing chlorides in presence of some bromide, is 215 heated, in a distillation flask, with hydrochloric acid and binoxide of manganese, the whole of the bromine passes over before any of the chlorine. Upon this circumstance, *Mohr* (Annal. d. Chem. u. Pharm., 93, 80) bases the following method for effecting the concentration of bromine.

Distil as stated, and conduct the vapors, through a double-bent tube, into a wide *Woulf's* bottle, which contains some strong solution of ammonia. Dense fumes form in the bottle, filling it gradually. Conduct the excess of vapors from the first into a second bottle, with narrow neck, which contains ammoniated water. Both bottles must be sufficiently large to allow no vapors to escape. When the whole of the bromine is evolved, which may be distinctly seen by the color of the space above the liquid in the distillation flask and tubes, raise the cork, to prevent the receding of bromide of ammonium fumes. Let the apparatus cool, and unite the contents of the 2 bottles; the fluid contains the whole of the bromine, and a relatively small portion of the chlorine.

b. Instead of treating the mixed chloride and bromide of silver 216 in a current of chlorine as in *a*, it may also be reduced to metallic silver, in a current of hydrogen. After accurately determining the weight of the reduced metal, calculate the amount of chloride of silver equivalent to it, subtract from this the weight of the chloride and bromide of silver subjected to the reducing process, and multiply the difference by 4·223, as in *a* (**212**). *Wackenroder.* It will be seen that one and the same portion of mixed bromide and chloride of silver may be treated first as directed in *a* (**212**), then, by way of control, as directed in *b*. The difference found in the direct way in the first, and by calculation in the second experiment, between the weight of the mixed chloride and bromide of silver and the amount of chloride of silver equivalent to it, must be the same.

c. Fr. Mohr ("Annal. d. Chem. u. Pharm.," 93, 76) recommends 217 to precipitate by a known quantity of silver the bromine and part of the chlorine, and to weigh the mixed precipitate of chloride and bromide of silver; which will of course again furnish the same bases for calculation as in *b* (**216**). The known quantity of silver used as precipitant is either weighed in the direct way, and dissolved in nitric acid, or added in form of a solution of nitrate of silver of known strength. This method is more convenient than the process described in *a* (**212**); but I do not consider it quite so accurate, more particularly for small quantities of bromine. It presupposes that a weighed quantity of silver will give an absolutely corresponding amount of chloride of silver, which practically is not the case, errors to the extent of some milligrammes being scarcely avoidable; it may accordingly happen that bromine is calculated from the supposed difference, even in cases where there is absolutely none present. Now the method *a* (**212**) is not so liable to lead to such mistakes, at least not to the same extent. On the contrary, a simple experiment will show that pure chloride of silver, heated cautiously, in a bulb-tube or porcelain boat, in a current of chlorine, suffers no alteration of weight; an error occurring in this operation to the extent of ½ milligramme is less excusable than one to the extent of 2 milligrammes, arising in the conversion of 2 or 3 grammes of silver into chloride, more especially if a filter is required in the process; and this can hardly ever be dispensed with in a partial precipitation, as, in such cases, the precipitate always subsides less readily and completely than in cases of full and complete precipitation.

d. Pisani's method ("Compt. rend.," 44, 352; "Journ. f. prakt. Chem.," 72, 266) may be looked upon as a modification of *c* (**217**). That chemist recommends to add a known quantity of solution of nitrate of silver in slight excess, filter, and determine the silver in the filtrate by iodide of starch (**139**). The precipitate is weighed as in *c*. This method precludes the partial precipitation. **218**

e. Determine in a portion of the solution the chlorine + bromine (by precipitating with solution of nitrate of silver), either gravimetrically or volumetrically; in another portion the bromine, either by the colorimetric method (§ 143, I., *b*), or by the volumetrical method (§ 143, I., *c*). Calculate the chlorine from the difference. This method is very suitable for an expeditious analysis of mother-liquors. **219**

2. CHLORINE FROM IODINE.

a. Mix the solution with nitrate of protoxide of palladium, and determine the precipitated protiodide of palladium as directed §145, I, *b*. Conduct sulphuretted hydrogen into the filtrate, to remove excess of the palladium, destroy the excess of sulphuretted hydrogen by solution of sulphate of sesquioxide of iron, and precipitate the chlorine finally with solution of nitrate of silver. It is generally found more simple and convenient to divide the solution into two parts, and precipitate from one portion the iodine, by means of protochloride of palladium, as directed § 145, I., *b*, from the other portion, the chlorine and iodine jointly with solution of nitrate of silver, and to calculate the chlorine from the difference. If you have no solution of nitrate of protoxide of palladium ready, and the chlorine and iodine must be determined jointly in a portion of the solution under examination, add a measured quantity of a solution of protochloride of palladium, determine the amount of chlorine in this in another exactly equal portion of the same solution, and deduct this. The results are accurate. **220**

In the case of fluids containing a large proportion of chlorides of the alkali metals, to a small quantity of iodides of the alkali metals, the iodide is concentrated by adding carbonate of soda to the fluid, evaporating to dryness, treating the residue with alcohol, evaporating the alcoholic solution, with addition of a drop of solution of soda, and treating the residue with water.

b. Precipitate a portion of the fluid with solution of nitrate of silver, and determine the chlorine + iodine; in another portion, determine the quantity of the iodine separately by the volumetrical method (§ 145, I., *d*, or *e*); calculate the chlorine from the difference. 221

c. Proceed exactly as for the indirect determination of bromine in presence of chlorine (**212**). The loss of weight suffered by the silver precipitate in the fusion in chlorine gas, multiplied by 2·569, gives the quantity of the iodide of silver decomposed by chlorine. The methods described in **216**, **217**, and **218**, may also be employed. The results obtained by these methods in the case of chlorine and iodine are still more accurate than in the case of chlorine and bromine, as the difference between the equivalents of iodine and chlorine is much greater than between those of chlorine and bromine. 222

d. Moride's Method ("Compt. rend.," 35, 789; "Journ. f. prakt. Chem.," 58, 317). Free iodine dissolves in benzole, imparting a red color to the fluid; this color is the darker, the greater the quantity of iodine dissolved; upon exposure to the air, the iodine volatilizes, and the fluid loses its color. If, therefore, a fluid containing an iodide of an alkali metal is mixed with a few drops of red fuming nitric acid and 2 or 3 grammes of benzole, and the mixture vigorously shaken, the benzole ascends to the surface, exhibiting a magnificent color. To determine the quantity of the iodine, the iodized benzole is washed with water, sulphurous acid added, drop by drop, with shaking, until the fluid is decolorized; then solution of nitrate of silver, the precipitate digested with nitric acid, the iodide of silver washed with alcohol, and determined in the usual way. Chlorine imparts no color to benzole, and remains dissolved in the water with which the benzole is washed. It is precipitated with solution of nitrate of silver. 223

e. The separation of iodine from chlorine may be effected also by means of bisulphide of carbon (or chloroform), as follows:—Mix the solution with a few drops of a solution of hyponitric acid in sulphuric acid, or with a few drops of red fuming nitric acid, add 4 or 5 grammes of bisulphide of carbon, shake vigorously, and separate the violet-colored bisulphide of carbon, by careful decantation, from the fluid, which contains the chlorine (and bromine). Wash carefully by decantation, then add dilute chlorine water, drop by drop, with shaking, until the color just disappears, which is a sign that the whole of the iodine is converted into ICl_5. Separate the solution from the bisulphide of carbon, add solution of iodide of potassium in sufficient excess, and determine the liberated iodine as directed § 146, 1 or 3. 224

Six parts of the iodine found correspond to 1 part of iodine originally present. If you wish to avoid the decantation and washing of the bisulphide of carbon, transfer the fluid, mixed with chlorine water to decolorization, to a rather narrow graduated cylinder, note the volume of the solution of the pentachloride of iodine (after deduction of the bisulphide of carbon), take out a portion with the pipette, and treat this as directed. The results which

I obtained by this process were satisfactory. The method is particularly suitable for the estimation of small quantities of iodine.

f. Add to the solution of the iodide and chloride ½ c.c. of solution of iodide of starch of known strength (**139**), then, drop by drop, with stirring, decimal standard solution of nitrate of silver (see § 115, at the end), until the iodide of starch is decolorized. The amount of silver solution used (after deducting the small quantity required for the decolorization of the ½ c.c. of iodide of starch solution added, and which must be separately determined) corresponds exactly to the amount of iodine in the analysed compound; for iodide of starch is decolorized before the precipitation of chlorine begins. To determine now the chlorine also, add again solution of nitrate of silver in slight excess, filter, and determine the excess of silver in the filtrate by means of iodide of starch (**139**). Deduct the amount of solution of nitrate of silver corresponding to the ½ c.c. of iodide of starch solution added, and to the iodine present, as well as the excess of silver solution from the total quantity added, and calculate the chlorine from the difference. This method is expeditious; the results are accurate (*Pisani*, "Compt. rend.," 44, 352; "Journ. f. prakt. Chem.," 72, 266). Compare also Analytical Notes and Experiments, No. 92. **225**

3. CHLORINE, BROMINE, AND IODINE FROM EACH OTHER.*

a. The three metalloids are determined jointly in a portion of the fluid, by precipitating with solution of nitrate of silver. To determine the iodine, another portion is precipitated with protochloride of palladium in the least possible excess. The fluid filtered from the precipitate is freed from palladium by means of sulphuretted hydrogen, and the excess of the latter removed by means of sulphate of sesquioxide of iron; the chlorine and bromine are then precipitated jointly, either completely or partially, with solution of nitrate of silver, and the bromine is finally determined as directed § 169, 1. **226**

If the compound contains a large proportion of chlorine to a small proportion of bromine, the iodine may be precipitated also by nitrate of protoxide of palladium, as there is no danger, in that case, of protobromide of palladium being thrown down with the precipitate. The filtrate is treated as above.

These methods give very accurate results; but they are applicable only if the quantity of iodide present is somewhat considerable.

b. Remove the iodine from the solution by bisulphide of carbon, or chloroform, as in **224**; but, in order to be quite sure that no bromine is liberated, use hyponitric acid, free from nitric acid.† (*Grange*, "Compt. rend.," 33, 627; "Journ. f. prakt. Chem.," 55, 167). In the fluid separated from the iodized bisulphide of carbon, determine the chlorine and bromine as directed in § 169, 1, and in the iodized bisulphide of carbon, the iodine as in **224**. This method is particularly recommended for the separation of small quantities of iodine, and in this respect is supplementary to **226**. **227**

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* The method recently recommended by *Fr. Field* ("Chem. Gaz.," 1857, No. 357), for the separation of chlorine, iodine, and bromine, rests on a false basis, as iodide of silver is sufficiently soluble in iodide of potassium solution, and bromide of silver in bromide of potassium solution, to give rise to very considerable mistakes.

† This may be obtained by a more intense ignition of feebly ignited nitrate of oxide of lead.

c. Determine in a portion of the compound the chlorine, bromine, 228
and iodine jointly by precipitation with nitrate of silver. Determine the silver in the weighed precipitate as in **216**. Or add a known quantity of solution of nitrate of silver in slight excess, filter, and determine the small excess of silver in the filtrate by means of iodide of starch (**218**).

Determine the iodine separately by *Dupré's* method (see below), calculate the quantity of iodide of silver and of silver corresponding to the amount of iodine found, deduct the calculated amount of iodide of silver from the mixed iodide, chloride, and bromide of silver, that of the silver from the known quantity of the metal contained in the mixed compound; the difference gives the joint amount of chloride and bromide of silver, on the one, the quantity of the metal contained in the bromide and chloride, on the other hand, and, accordingly, the basis for calculating the chlorine and bromine (**216**).

As regards the estimation of iodine in presence of bromides, *A.* and *F. Dupré* found that, if the solution of an iodide contains 1 part of bromide of potassium, or more, in 1500 parts of water, protobromide of iodine ($I\,Br$) is formed upon addition of chlorine water; if the solution contains less than 1 part of bromide of potassium in 1500 parts of water, higher bromides in varying proportions are formed in addition to the protobromide. If the solution contains only 1 part of bromide of potassium to 13,000 parts of water, pentabromide of iodine ($I\,Br_5$) alone is formed. If the iodine was dissolved in bisulphide of carbon, the conversion into $I\,Br$ is marked simply by the change of the violet color of the fluid to yellowish brown (Zirconium color), whereas the formation of $I\,Br_5$ is marked by the change of violet to white.

Upon these reactions *A.* and *F. Dupré* have based the following method :—Test the fluid first by adding bisulphide of carbon, then, gradually, chlorine water, to see whether the color will change from violet to white. If this is not the case, dilute to the required degree, and, to make quite sure, add one-half more water; then proceed as directed § 145, I., *d*, *α* or *β*. *A.* and *F. Dupré* obtained most satisfactory results by this process; the method is particularly recommended for the determination of small quantities of iodine.

d. Proceed generally as in *c* (**228**), but determine the iodine by 229
Pisani's method (**225**). This method also gives very satisfactory results. Presence of bromides does not interfere with the accuracy of the estimation of the iodine (Analytical Notes and Experiments, No. 93).

4. ANALYSIS OF IODINE CONTAINING CHLORINE.

a. Dissolve a weighed quantity of the dried iodine in cold sul- 230
phurous acid, precipitate with solution of nitrate of silver, digest the precipitate with nitric acid, to remove the sulphite of silver which may have precipitated along with the iodide and chloride, and then determine the weight of the precipitated silver salt. The calculation of the iodine and chlorine is made by the following equations, in which A represents the quantity of iodine analysed, x the iodine contained in it, y the chlorine contained in it, and B the amount of chloride and iodide of silver obtained :—

$$x + y = A, \text{ and}$$
$$\frac{Ag+I}{I}\,x + \frac{Ag+Cl}{Cl}\,y = B$$

But as

$$\frac{Ag+I}{I} = 1{\cdot}851$$

and

$$\frac{Ag+Cl}{Cl} = 4{\cdot}045$$

the result is

$$y = \frac{B - 1{\cdot}851\,A}{2{\cdot}194}$$

b. If you have free iodine and free chlorine in solution, determine in a portion, after heating with sulphurous acid, the iodine as iodide of palladium (§ 145, I., *b*), and treat another portion as directed § 146, 1. Deduct from the apparent amount of iodine found by the latter process, the actual quantity calculated from the iodide of palladium; the difference expresses the amount of iodine equivalent to the chlorine contained in the analysed compound. 231

5. ANALYSIS OF BROMINE CONTAINING CHLORINE.

a. Proceed exactly as in 230, weighing the bromine in a small glass tube. Taking *A* to be equal to the analysed bromine, *B* to the bromide and chloride of silver obtained, x to the bromine contained in *A*, y to the chlorine contained in *A*, the calculation is made by the following equations :— 232

$$x + y = A$$

and

$$y = \frac{B - 2{\cdot}35\,A}{1{\cdot}695}$$

b. Mix the weighed anhydrous bromine with solution of iodide of potassium in excess, and determine the separated iodine as directed § 146, 1. 233

From these data, the respective quantities of bromine and chlorine are calculated by the following equations. Let *A* represent the weighed bromine, i the iodine found, y the chlorine found in *A*, x the bromine contained in *A*, then

$$x + y = A$$
$$y = \frac{i - 1{\cdot}5866\,A}{1{\cdot}991}$$

Bunsen, the originator of methods 4 and 5, has proved their perfect accuracy by a series of successful experiments ("Annal d. Chem. u. Pharm.," 86, 274, 276).

6. CYANOGEN FROM CHLORINE, BROMINE, OR IODINE.

a. Precipitate with solution of nitrate of silver, collect the precipitate upon a weighed filter, and dry on the water-bath until the weight remains constant; then determine the cyanogen by the 234 method of organic analysis; the difference expresses the quantity of the chlorine, bromine, or iodine.

b. Precipitate with solution of nitrate of silver as in *a*, dry the precipitate at 212° F., and weigh. Heat the precipitate, or an aliquot part of it, in a porcelain crucible, with cautious agitation of the contents, to complete fusion; add dilute sulphuric acid to the fused mass, then reduce by zinc, filter the solution off from the metallic silver and paracyanide of silver, and determine the chlorine, iodine, and bromine in the filtrate, in the usual way by solution of nitrate of silver. *Neubauer* and *Kerner* ("Annal. d. Chem. u. Pharm.," 101, 344) obtained very satisfactory results by this method. 235

c. Determine the elements jointly in a portion of the solution, by precipitating with solution of nitrate of silver, and the cyanogen in another portion, by the volumetrical method (§ 147, I., *b* or *c*). 236

7. FERRO- OR FERRI-CYANOGEN FROM HYDROCHLORIC ACID.

To analyse ferro- or ferri-cyanide of potassium, &c., mixed with the chloride of an alkali metal, determine in one portion the ferro- or ferri-cyanogen as directed § 147, III.; acidify another portion with nitric acid, precipitate with solution of nitrate of silver, filter, wash the precipitate, fuse with 4 parts of carbonate of soda, and 1 part of nitrate of potassa, extract the fused mass with water, and determine the chlorine in the solution as directed in § 141. 237

8. SULPHURETTED HYDROGEN FROM HYDROCHLORIC ACID.

The usual method of separating the two acids by means of a metallic salt is liable to give false results, as part of the chloride of the metal may fall down with the sulphide. The safest way, therefore, is to precipitate both as silver compounds, dry the precipitate at 212° F., and determine the sulphur in a weighed portion; or, which is usually preferred, determine in a portion of the solution the sulphuretted hydrogen as directed § 148, in another portion the sulphur + chlorine in form of silver salts. To remove sulphuretted hydrogen from an acid solution, in order that chlorine may be determined in the latter by means of nitrate of silver, *H. Rose* recommends to add solution of sulphate of sesquioxide of iron, which will effect the separation of sulphur alone; the separated sulphur is allowed to deposit, and then filtered off. 238

THIRD GROUP.

NITRIC ACID—CHLORIC ACID.

I. SEPARATION OF THE ACIDS OF THE THIRD GROUP FROM THOSE OF THE FIRST TWO GROUPS.

§ 170.

a. If you have a mixture of nitric acid or chloric acid with another free acid in a fluid containing no bases, determine in one portion the joint amount of the free acid, by the acidimetrical method (see Special Part), in another portion the acid mixed with the chloric or nitric acid, and calculate the amount of either of the latter from the difference. 239

b. If you have to analyse a mixture of a nitrate or chlorate with some other salt, determine in one portion the nitric acid or chloric acid by the volumetrical method (§ 149, II., *a*, and § 150), or the nitric acid by means of arsenious acid (149, II., *b*); and in another portion the other acid. I think I need hardly remark that no substances must be present which would interfere with the application of these methods. **240**

c. From the chlorides of those metals which form with phosphoric acid insoluble tribasic phosphates, the salts of the acids of the third group may be separated also by digesting the solution with recently precipitated thoroughly washed tribasic phosphate of silver, and boiling the mixture. In this process, the chlorides transpose with the phosphate—chloride of silver and phosphate of the metal with which the chlorine was originally combined being formed, which both separate, together with the excess of the phosphate of silver, whilst the chlorates and nitrates remain in solution (*Chevenix; Lassaigne*, "Journ. de Pharm.," 16, 289; "Pharm. Centralbl.," 1850, 121). **241**

d. The estimation of the chloric acid in a chlorate, in presence of the chloride of an alkali metal, may be effected also in the following manner:—A weighed portion of the compound is precipitated from the aqueous solution with nitrate of silver, and the precipitated chloride of silver accurately weighed; an equal portion of the substance is cautiously ignited, the residue dissolved in water, nitrate of silver added in excess to the solution, and the precipitated chloride of silver weighed. The quantity of the chloric acid is then calculated from the difference in the weight of the two precipitates. **242**

II. SEPARATION OF THE ACIDS OF THE THIRD GROUP FROM EACH OTHER.

We have as yet no method to effect the direct separation of nitric acid from chloric acid; the only practicable way, therefore, is to determine the two acids jointly in a portion of the compound, either by the method given § 149, II., *a*, *a*, or by § 149, II., *b*; and in another portion the chloric acid, by adding carbonate of soda in excess, evaporating to dryness, fusing the residue until the chlorate is completely converted into chloride, and then determining the chlorine in the latter; 1 equivalent of chloride of silver produced from this corresponds to 1 equivalent of chloric acid, provided there was no chlorine originally present. **243**

SECTION VI.

ELEMENTARY OR ULTIMATE ANALYSIS OF ORGANIC BODIES.

§ 171.

ORGANIC compounds contain only comparatively few of the elements which constitute the material world. A small number of them consist simply of 2 elements, viz.,

C and H;

the greater number contain 3 elements, viz., usually,

C, H, and O;

most of the rest 4 elements, viz., generally,

C, H, O, and N;

a small number 5 elements, viz.,

C, H, O, N, and S;

and a few, 6 elements, viz.,

C, H, O, N, S, and P (?).

This applies to all the natural organic compounds which have as yet come under our notice. But we may *artificially* prepare organic compounds containing other elements besides those enumerated; thus we know many organic substances, the radicals of which contain chlorine, iodine, or bromine; or arsenic, antimony, tin, zinc, platinum, iron, cobalt, &c., &c.; and it is quite impossible to say which of the other elements may not be similarly capable of forming constituents of organic compounds (constituents of organic radicals).

With these compounds we must not confound those in which organic acids are combined with inorganic bases, or organic bases with inorganic acids, such as tartrate of lead, for instance, silicate of oxide of ethyle, borate of morphia, &c.; since in this class of compounds, of course, all and any of the elements may happen to be present.

Organic compounds may be analysed either with a view simply to resolve them into their proximate constituents; thus, for instance, a gum resin is resolved into resin, gum, and ethereal oil;—or the analysis may have for its object the determination of the absolute and relative weight of the ultimate constituents (the elements) of the analysed compound. The simple resolution of organic compounds into their proximate constituents is effected by methods perfectly similar to those used in the analysis of inorganic compounds; that is, the operator endeavors to separate (by solvents, application of heat, &c. &c.) the individual constituents from one another, either in the *direct* way, or after having previously converted them into appropriate forms. We disregard here altogether this branch of organic analysis—of which the methods must be nearly as numerous and varied as the cases which require their application—and proceed at once to treat of the second branch, which, to distinguish it from the other, is called *Elementary* or *Ultimate Analysis of Organic Bodies.*

The ultimate analysis of organic bodies has accordingly, as stated above, for its object the determination of the absolute and relative weight of the individual elements of organic compounds. It teaches us how to convert these elements into compounds of known composition, to separate the new compounds formed from one another, to weigh these, and to calculate from the results the quantities of the separate elements. Organic analysis, therefore, is based upon the same principle upon which rest most of the methods of separating and determining inorganic compounds.

The decomposition of most organic substances into distinctly characterized and readily separable products, which will permit an accurate determination of weight, offers no great difficulties, and organic analysis is therefore usually one of the more easy tasks of analytical chemistry;—and as, from the limited number of the elements which constitute organic bodies, there is necessarily a great sameness in the products of their decomposition, the analytical process is always very similar, and a few methods suffice for all cases. It is principally ascribable to this latter circumstance that organic analysis has so speedily attained its present high degree of perfection :—the constant examination and improvement of a *few* methods by a *great number* of chemists could not fail to produce this result.

Organic analysis may have for its object either simply to ascertain the *relative* proportion of the constituent elements of a substance,—thus, for instance, woods are analysed to ascertain their value as fuel, fats to ascertain their capacity of furnishing light—or to determine not only the *relative proportions* of the constituent elementary atoms, but also their *absolute quantity*, that is, to determine the exact number of equivalents of carbon, hydrogen, oxygen, &c. &c., which constitute 1 equivalent of the analysed compound. In scientific investigations we have invariably the latter object in view, although not yet able to achieve it in all cases. These two distinct objects cannot well be attained by one and the same operation; each requires a different and distinct process.

The methods by which we ascertain the relative proportions of the constituent elements of organic compounds, may be called collectively, "*elementary* or *ultimate analysis of organic bodies,*" in a more restricted sense; whilst the methods which reveal to us the *absolute number* of elementary equivalents constituting the complex equivalent of the analysed compound, may be styled "*determination of the equivalents of organic bodies.*"

The success of an organic analysis depends upon two conditions; viz., 1, upon the selection of the proper method; and, 2, upon the correct performance of the necessary operations and processes: expertness in this branch may be readily acquired by any one endowed with some patience, clearness of perception, and skill in chemical manipulation. The selection of the method depends upon the knowledge of the constituents of the compound under examination, and the method selected will always require certain modifications, according to the different properties and state of aggregation of these constituents. Before we can proceed, therefore, to describe the various methods applicable in the different cases that may occur, we have first to occupy ourselves here with the general means of ascertaining the constituent elements of organic bodies.

I. QUALITATIVE EXAMINATION OF ORGANIC BODIES.

§ 172.

It is not necessary for the correct selection of the proper method, to know all and every one of the elements of an organic compound, since the presence or absence of some of them—of oxygen, for instance—has not the slightest modifying influence upon the manner of proceeding with the analysis. But with regard to other elements, such as nitrogen, sulphur, phosphorus, chlorine, iodine, bromine, &c. &c., and also the various metals, it is absolutely indispensable that the operator should know positively whether either of them is present. This may be ascertained in the following manner:—

1. *Testing for Nitrogen.*

Substances containing a tolerably large amount of nitrogen exhale upon combustion, or when intensely heated, the well-known smell of singed hair or feathers. No further test is required if this smell is distinctly perceptible; otherwise the following experiments are resorted to:—

a. The substance under examination is mixed with hydrate of potassa in powder, or with *soda-lime* (§ 66, 5), and the mixture heated in a test-tube. If the examined substance contains nitrogen, ammonia will be evolved, which may be readily detected by its peculiar odor, by its reaction upon vegetable colors, and by the formation of white fumes when brought into contact with volatile acids. Should these reactions fail to afford positive proof of the presence of nitrogen, every doubt may be removed by the following experiment:—Heat a somewhat larger portion of the substance, in a short tube, with an excess of *soda-lime*, and conduct the products of the combustion into dilute hydrochloric acid; evaporate the acid on the water-bath, dissolve the residue in a little water, and mix the solution with bichloride of platinum and alcohol. Should no precipitate form, even after the lapse of some time, the examined substance may be considered free from nitrogen.

b. Lassaigne has recently proposed another method, which is based upon the property of potassium to form cyanide of potassium when ignited with a nitrogenous organic substance. The following is the best mode of performing the experiment:—

Heat the substance under examination, in a test-tube, with a small lump of potassium, and after the complete combustion of the whole of the potassium, treat the residue with a little water (cautiously); filter the solution, add 2 drops of solution of sulphate of protoxide of iron containing some sesquioxide, digest the mixture a short time, and add hydrochloric acid in excess. The formation of a blue or bluish-green precipitate or coloration proves the presence of nitrogen.

Both methods are delicate; *a* is the one most generally employed; it fully answers the purpose in nearly all cases.

c. In organic substances containing oxides of nitrogen, the presence of nitrogen cannot be shown by either *a* or *b*, but it may be readily detected by heating the substance in a tube, when the evolution of red acid fumes, imparting a blue tint to iodide of starch paper, will incontestably prove it.

2. *Testing for Sulphur.*

a. Solid substances are fused with about 12 parts of pure hydrate of potassa, and 6 parts of nitrate of potassa. Or they are intimately mixed with some pure nitrate of potassa and carbonate of soda; nitrate of potassa is then heated to fusion in a porcelain crucible, and the mixture gradually added to the fusing mass. The mass is allowed to cool, then dissolved in water, and the solution tested with baryta, after previously acidifying with hydrochloric acid.

b. Fluids are treated with fuming nitric acid, or with a mixture of nitric acid and chlorate of potassa, at first in the cold, finally with application of heat; the solution is tested as in *a.*

c. As the methods *a* and *b* serve simply to indicate the presence of sulphur in a general way, but afford no information regarding the state or form in which that element may be present, I add here another method, which serves to detect only the sulphur in the non-oxidized state in organic compounds.

Boil the substance with strong solution of potassa, and evaporate nearly to dryness. Dissolve the residue in a little water, pour the solution into the flask *A* (Fig. 81), and slowly add dilute sulphuric acid through the funnel-tube *c*; if sulphur is present, the slip of paper *b*, which has been thoroughly moistened with solution of acetate of lead, and then touched with a few drops of solution of carbonate of ammonia, will turn brown. I need hardly mention that the cork must not fit air-tight into the mouth of *A*. Instead of in the manner described, the sulphide of potassium formed may be detected also by means of nitroprusside of sodium, or by just acidifying the dilute solution with hydrochloric acid, and adding a few drops of a mixture of sesquichloride of iron, and ferricyanide of potassium (See "Qual. Analysis," § 156).

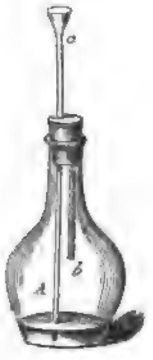

Fig. 81.

3. *Testing for Phosphorus.*

The methods described in 2, *a*, and *b*, may likewise serve for phosphorus. The solutions obtained are tested for phosphoric acid with sulphate of magnesia; or with sesquichloride of iron, with addition of acetate of soda; or with molybdate of ammonia (compare "Qualitative Analysis"). In method *b*, the greater part of the excess of nitric acid must first be removed by evaporation.

4. *Testing for Inorganic Substances.*

A portion of the substance under examination is heated on platinum foil, to see whether or not a residue remains. When acting upon difficultly combustible substances, the process may be accelerated by heating the spot which the substance under examination occupies on the platinum foil, to the most intense redness, directing the flame of the blowpipe upon the corresponding point of the lower surface of the foil. The residue is then examined by the usual methods. That volatile metals in volatile organic compounds—*e.g.*, arsenic in kakodyl—cannot be detected by this method, need hardly be mentioned.

These preliminary experiments should never be omitted, since neglect in this respect may give rise to very great errors. Thus, for instance, *taurine*, a substance in which a large proportion of sulphur was afterwards found to exist, had originally the formula $C_4\,N\,H_7\,O_{10}$ assigned for its composition. The preliminary examination of organic substances for chlorine, bromine, and iodine, is generally unnecessary, as these elements do not occur in native organic compounds; and as their presence in compounds artificially produced by the action of the salt-radicals requires generally no further proof. Should it, however, be desirable to ascertain positively whether a substance does or does not contain chlorine, iodine, or bromine, this may be done by the same methods which we shall have occasion to describe in the quantitative determination of organic compounds.

II. QUANTITATIVE DETERMINATION OF THE ELEMENTS IN ORGANIC BODIES.

It is not my intention to give an account of the rise and progress of the science of organic analysis; I shall therefore confine myself to the description of the most simple, precise, and universally applicable methods, omitting all the rest. The more simple methods, which may be performed by way of practice, will be most fully described; the more complicated methods, which presuppose a more advanced knowledge of the general manipulations of organic analysis, will be given more briefly.

The accuracy of the results depends both upon the appropriate construction and arrangement of the apparatus required for the various analytical processes, and upon the proper execution of these processes. I am anxious, therefore, to impress upon the student the necessity of bestowing equal attention and diligence upon both; the rules which I have laid down are the fruits of long experience and of innumerable experiments.

A. ANALYSIS OF COMPOUNDS WHICH CONSIST SIMPLY OF CARBON AND HYDROGEN, OR OF CARBON, HYDROGEN, AND OXYGEN.

§ 173.

The principle of the method which serves to effect the quantitative analysis of such compounds, and which owes its present perfection to Professor *Liebig*, is exceedingly simple. The substance under examination is burned, and thus converted into carbonic acid and water; these products are then separated from each other and weighed, and the carbon of the analysed substance is calculated from the weight of the carbonic acid, the hydrogen from that of the water. If the sum of the calculated weight of the carbon and hydrogen is equal to the original weight of the substance, the absence of oxygen is at once satisfactorily proved; should the sum, on the other hand, be less than the original weight of the substance, the difference will at once indicate the amount of oxygen originally present in the analysed compound.

The combustion is effected either by igniting the organic substance with oxygenized bodies which readily part with their oxygen (oxide of copper, chromate of lead, &c. &c.); or by means of free oxygen gas; or, finally, at the expense both of free and combined oxygen.

[NOTE.—The only attempt at determining the oxygen in organic bodies in the direct way, has been made by *Baumhauer* ("Annal. d. Chem. u. Pharm.," 90, 228).

The following is the process given by this chemist:—Mix the organic substance with oxide of copper, in the usual way, and heat in a glass tube open at both ends. Collect the carbonic acid and the water in the usual way. The two ends of the apparatus are connected with accurately graduated glass-tubes, of which the one at the posterior end is filled with oxygen gas. At the termination of the process of combustion, this oxygen gas is passed over the ignited oxide of copper and reduced copper, by which means the reduced metal is reoxidized. Allow the apparatus to cool, read off the volume of gas in the two graduated tubes (as has been done also before the process), and then determine the weight of the carbonic acid and water. Make due correction for the state of the barometer and thermometer, then deduct the volume of gas found in the two tubes after the combustion, from the volume before the process; the difference gives the quantity of oxygen absorbed by the reduced copper. Deduct now this difference from the joint amount of oxygen in the carbonic acid and water formed; the difference gives the quantity of oxygen in the analysed substance. As the total amount of gas in the apparatus cannot be accurately known, the results of the operation can only be expected to be correct if nearly the same pressure and temperature are maintained at the end as at the beginning of the experiment; there must also be no alteration in the volume of the tube. *Baumhauer* analysed oxalic acid and oxalate of lead by this method, with the following most satisfactory results:—

0·9895 grm. of oxalic acid gave 0·969 of carbonic acid and 0·203 of water. The total volume of gas in the apparatus, duly corrected, was, before the process, 485·90 c.c., after the process 360·33 c.c. Calculating from this the per-centage composition of oxalic acid, we have

		Calculated.	Found.
Carbon	12	26·66	26·71
Hydrogen	1	2·23	2·28
Oxygen	32	71·11	71·32
	45	100·00	100·31

The analysis of oxalate of lead gave 16·30 per cent. of oxygen, instead of 16·26, as theoretically calculated.]

a. SOLID BODIES.*

a. Readily combustible, non-volatile substances (*e.g.*, sugar, starch, tartaric acid, and the far greater number of solid organic bodies).

1. *Liebig's Method.*

I. APPARATUS AND PREPARATIONS REQUIRED FOR ORGANIC ANALYSIS.

§ 174.

The following is a complete list of everything requisite for the performance of an organic analysis:—

1. THE SUBSTANCE INTENDED FOR ANALYSIS. — This must be most finely pulverized and perfectly pure and dry;—for the method of drying organic substances, I refer to § 26.

2. A TUBE IN WHICH TO WEIGH THE SUBSTANCE.—A small perfectly dry glass tube, about 4 or 5 centimetres long, and about 1 centimetre wide, is used for this purpose; the weight of tube must be accurately determined to within a centigramme. It is advisable to place the tube in the drying

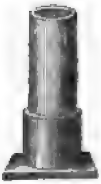

Fig. 82.

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* For the analysis of fats, waxy bodies, &c., which cannot be reduced to powder, I refer to § 182.

apparatus, together with the substance intended for analysis. On the balance the tube is appropriately placed in a little foot made of tin (Fig. 82).

3. A COMBUSTION TUBE.—A tube of difficultly fusible glass (potassa glass), about 2 millimetres thick, 90 centimetres in length, and from 12 to 14 millimetres inner diameter, is softened in the middle before a glassblower's lamp, drawn out as represented in Fig. 83, and finally cut in two at *b*. The fine points of the two pieces are then thickened a little and sealed in the flame, and the sharp edges of the open ends, *a* and *c*, are slightly rounded by fusion, care being taken to leave the aperture perfectly round; and also to have the pointed end of the tube shaped as shown in Fig. 84, and not as in Fig. 85.

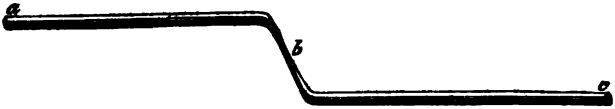

Fig. 83.

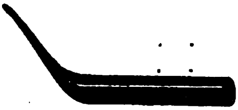

Fig. 84.

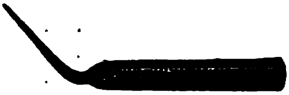

Fig. 85.

Two perfect combustion tubes are thus produced. The one intended for immediate use, is cleaned with a linen or paper-wiper attached to a piece of wire, and then thoroughly dried. This is effected either by laying the tube, with a piece of paper twisted over its mouth, for some time on the plate of a common stove, or on a sand-bath, with occasional removal of the air from it by suction, with the aid of a glass-tube, or, in cases where it is desirable to lose no time, by moving the tube to and fro over the flame of a spirit-lamp, in its entire length, continually removing the hot air by suction through the glass-tube (Fig. 86).

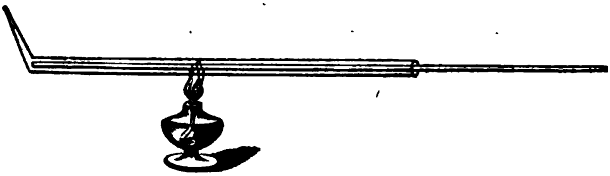

Fig. 86.

The combustion tube, when quite dry, is closed air-tight with a perfectly dry cork, and kept in a warm place until required for use.

In default of glass-tubes possessed of the proper degree of infusibility, a thin sheet of copper is rolled round the tube, and iron wire coiled round it.

4. A (LIEBIG'S) POTASSA-APPARATUS (illustrated by Fig. 87), which may be readily procured from any maker of chemical instruments, or glass-blower. This apparatus is filled to the extent indicated in the engraving, with a clear solution of caustic potassa of 1·27 sp. gr., which should be as free as possible from carbonate of potassa (§ 66, 8). The introduction of the solution of potassa into the apparatus is effected by plunging the end *a* (but on no account the other end) into the vessel which contains the solution of potassa, and applying suction to *b*, either by means of a caoutchouc tube, or (and this is the safest way) with the aid of a small suction tube (applied as in Fig. 88). The two ends are then wiped perfectly dry with twisted slips of paper, and the outside of the apparatus with a clean cloth.

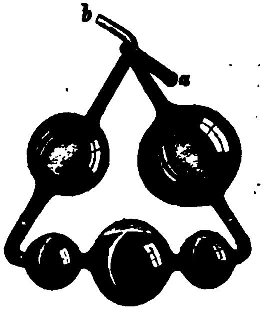

Fig. 87.

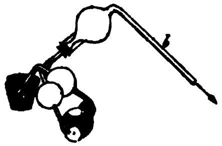

Fig. 88.

5. A CHLORIDE OF CALCIUM TUBE (Fig. 89), which may also be purchased. This tube is filled in the following manner:—In the first place, the aperture *a* of the tube *b a* is loosely stopped with a small cotton plug, reaching about one centimetre into the tube; this is effected by introducing a very loose cotton plug into *c*, and applying a sudden and energetic suction at *b*. The bulb of the tube is then filled with lumps of chloride of calcium (§ 66, 9, *b*), and the tube *c d* up to *e* with smaller fragments, intermixed with coarse powder of the same substance; a loose cotton plug is then inserted, and the tube finally closed with a perforated cork, into which a small glass tube is fitted; the protruding part of the cork is cut off, and the cut surface covered over with sealing-wax; the edge of the little tube *f g* is slightly rounded at *g* by fusion (see Fig. 90).

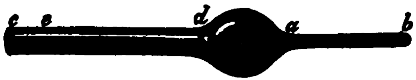

Fig. 89.

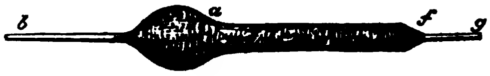

Fig. 90.

The tube illustrated by Fig. 91, is still better adapted for the purpose —at least in most cases (for substances containing no sulphur)—as its construction enables the operator to test, after the experiment, the reaction, &c., of the water condensed in the empty bulb *a*. It afford also the advantage that it may be much more frequently used without requiring a new filling than a tube not provided with an empty bulb.

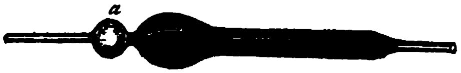

Fig. 91.

6. A SMALL TUBE OF VULCANIZED INDIA-RUBBER.—This must be so

narrow that it can only be pushed with difficulty over the tube *g* of the chloride of calcium apparatus on the one, and over the end *a* of the potassa-apparatus on the other hand; in which case there is no need of binding with silk cord. If the vulcanized india-rubber tube should be a little too wide, it must be tied round with silk cord. It is self-evident that the tube *g* of the chloride of calcium apparatus and the tube *a* of the potassa apparatus should be of the same width. The india-rubber tube is dried in the water-bath previous to use.

7. Cork Stoppers.—Soft and smooth corks, as free as possible from visible pores, are best adapted for the purpose; a cork should be selected which fits perfectly tight, and screws with some difficulty to one-third of its length, at the most, into the mouth of the combustion tube; a perfectly smooth and round hole, of the same diameter as the end *b a* of the chloride of calcium tube, is then carefully bored through the axis of the cork by means of a fine round file; into this perforation the end *b a* of the chloride of calcium tube must fit perfectly air-tight. The cork is then dried in the water-bath. It is advisable always to have two corks of this description ready. *Sonnenschein* ("Journ. f. prakt. Chem.," 67, 153) recommends stoppers of vulcanized india-rubber, made of perforated cylinders of that substance; he says they are lasting, fit tight, and are not hygroscopic. I cannot as yet pronounce on the subject from experience.

8. A Mortar for Mixing.—A porcelain mortar, of greater width than depth, should be selected; it must be provided with a lip, and free from indentations and fissures, and should not be glazed inside. Previous to use, it is washed with water, allowed to dry in a warm place, and left there till required.

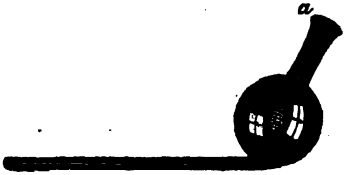

Fig. 92.

9. A Suction Tube.—Fig. 92 illustrates the most appropriate form of a suction tube.

The aperture *a* is closed with a perforated cork, into which the tube *b* of the potassa-apparatus is fitted. A caoutchouc tube may be advantageously used instead of a perforated cork.

10. A glass tube, open at both ends, about 60 centimetres long, and of sufficient width to admit being pushed over the pointed end of the combustion tube, where it is kept in position by supporting it against the arm of a filtering stand (see Fig. 100).

11. A sheet of glazed paper, with cut edges.

12. A Liebig's Combustion Furnace, of sheet iron, with a single and a double screen. It has the form of a long box, open at the top and after part. It serves to heat the combustion tube with red-hot wood charcoal. Fig. 93 represents the furnace as seen from the top.

Fig. 93.

It is from 50 to 60 centimetres long, and from 7 to 8 deep; the bottom, which, by cutting small slits in the sheet iron, is converted into a grating, has a width of about 7 centimetres. The side walls are inclined slightly outward, so that at the top they stand about 12 centimetres apart. The furnace is furnished with a series of upright pieces of strong sheet iron, of equal height, of the form shown in Fig. 94, *D*, which are fastened upon the bottom of the furnace, at intervals of about 5 centimetres. These pieces serve to support the combustion tube. They must be of exactly corresponding height with the round aperture in the front piece of the furnace (Fig. 94, *A*).

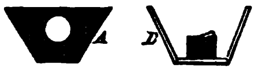

Fig. 94.

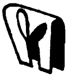

Fig. 95.

This aperture must be sufficiently large to admit the combustion tube easily. Of the two screens, the one has the form shown in Fig. 95, the other that shown in Fig. 94, *A*, with the border turned down at the upper edge. The openings cut into the screens must be sufficiently large to receive the combustion tube without difficulty. The furnace is placed upon flat bricks resting upon wood, and is slightly raised at the farther end, by inserting a piece of wood between the supports (see Fig. 98). The apertures of the grating at the anterior end of the furnace must not be blocked up by the supporting bricks. In cases where the combustion tubes are of a good quality, the furnace may be raised more advantageously by introducing a little iron rod or a piece of a tile between the furnace and the supporting brick; this arrangement will give the air free access to all the holes of the grating; or the furnace may also be directly placed upon a tripod—which, in fact, is now the usual way. Placing the tube in a gutter of very thin sheet iron tends greatly to preserve it.*

13. Oxide of Copper.—A hessian crucible, of about 100 c.c. capacity is nearly filled with oxide of copper prepared as directed in § 66, 1; the crucible is covered with a well-fitting overlapping lid, and heated to dull redness; it is then allowed to cool, so that by the time the oxide of copper is required for use, the hand can only just bear contact with it.

14. An exhausting Syringe with Chloride of Calcium Tube.—See Fig. 97. For the manner of performing an organic analysis without the aid of this apparatus, I refer to §§ 176, 177, 179.

15. Hot Sand.—The temperature of this should exceed 212° F., but must not be sufficiently high to singe paper.

16. A wooden Trough for the sand.—See Fig. 97.

II. Performance of the Analytical Process.

§ 175.

a. Weigh first the potassa-apparatus, then the chloride of calcium tube.

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* Coal-gas is now used in many laboratories as a source of heat, instead of charcoal; different forms of apparatus have been devised for the purpose by several chemists, as by *Baumhauer* ("Annal. d. Chem. u. Pharm.," 90, 21); *Hofmann* (Ibid., 90, 235); *Sonnenschein* ("Journ. f. prakt. Chem.," 55, 478); *Magnus* (Ibid., 60, 32); *Lehmann* "Polyt. Centralbl.," 1857, 609); Wetherill (*Liebig u. Kopp's* "Ann. Rep.," 1855, 828); *Pebal* ("Annal. d. Chem. u. Pharm.," 95, 24), &c. Until time and experience shall have tested the respective merits of the several apparatus proposed, I must content myself with referring the reader to the papers on the subject. A description of Hofmann's gas-furnace will be found page 488.

Introduce about 0·350—0·600 grm. (more or less according as the substance under examination is rich or poor in oxygen) into the little tube* (I., 2), which must be no longer warm, and weigh the latter accurately with its contents. The weight of the empty tube being known, it is easy to take the right quantity of substance required for the analysis. Close the tube then with a smooth cork, covered over the bottom and sides with tin foil.

b. Spread the sheet of glazed paper (I., 11) upon a clean table, and place the still moderately warm mortar (I., 8) on it. Rinse both the mortar and the still warm combustion tube with a little of the hot oxide of copper;† then fill the combustion tube up to *b* (see Fig. 96) with oxide of copper, either using the tube itself to take up the oxide with, or transferring the latter from the crucible to the tube with the aid of a small warm copper funnel and a teaspoon of German silver. Transfer a portion of the oxide of copper from the tube to the mortar, add the substance intended for analysis from the small tube in which it has been weighed, taking care to shake out, as far as practicable, the last adhering particles of the substance; put by the empty small tube carefully, as you will have to re-weigh it. Mix the substance and the oxide in the mortar most intimately together, taking care to avoid a too energetic pressure upon the pestle; add to the mixture nearly all the oxide of copper still in the tube, leaving only a layer of about 3 or 4 centimetres in the latter; and mix the whole most intimately together. Take the pestle out of the mortar, shaking off as clean as possible the minute particles of the mixture adhering to it; transfer the greatest part of the contents of the mortar to the tube, employing the latter itself for the purpose; place the rest of the mixture on a smooth card, and pass it from this into the tube; rinse the mortar with a little more oxide of copper from the crucible, and put this also into the tube, which will now be full to about *a* (Fig. 96); fill up to within 3 or 4 centimetres from the mouth with pure oxide of copper from the crucible, and close the tube temporarily with a dry cork. The reason why the operation of filling the tube is conducted over the sheet of glazed paper is that, should any of the mixture be spilled, this may be readily recovered.‡

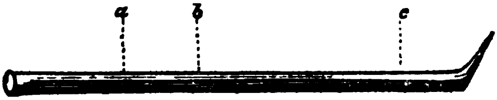

Fig. 96.

c. A few gentle taps on the table will generally suffice to shake together the contents of the tube, so as to completely clear the pointed end from oxide of copper, and leave a free passage for the evolved gases from end to end, as shown by the shading in the cut. Should this fail, as will occasionally happen, owing to malformation of the beak, the object in view may be attained by striking the mouth of the tube several times against the side of a table. Place the tube now into the wooden trough *D* (Fig. 97), connect it by a cork with the chloride of calcium tube *B*, and the latter again with an exhausting syringe. Surround the combustion tube in its whole length with hot sand (I., 15),

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* Care must be taken that no particles of the substance adhere to the sides of the tube, at least not at the top.

† The oxide which has served for this purpose is put by.

‡ In *Mulder's* laboratory, I saw the operation of filling performed in a different, but certainly very easy and expeditious way. The combustion tube was placed upright in a retort holder, and the mixture, which had been made in a small copper dish, filled in through a smooth, warm copper funnel.

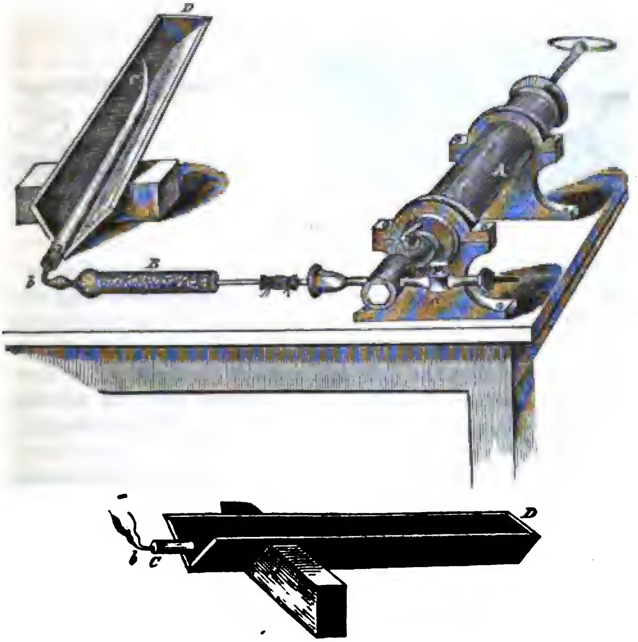

Fig. 97.

and pump out the air *slowly* (quick and incautious pumping might cause a portion of the mixture to pass into the chloride of calcium tube). Open the stopcock *a*, to admit a fresh supply of air, which is completely dried in its passage through the chloride of calcium tube; exhaust again, re-admit fresh air, and repeat this process of alternate exhaustion and re-admission of air 10 or 12 times, which will ensure the perfect removal of the moisture which the oxide of copper may have absorbed during the operation of mixing.

d. Connect the end *b* of the weighed chloride of calcium tube (I., 5) with the combustion tube by means of a dried perforated cork (I., 7); lay the furnace upon its supports, with a slight inclination forward, and place the combustion tube in it; connect the end *β* of the chloride of calcium tube, by means of a vulcanized india-rubber tube (I., 6), with the end *m* of the potassa-apparatus, and, if necessary, secure the connection with silk cord, taking care to press the balls of the two thumbs close together whilst tightening the cords, since otherwise, should one of the cords happen to give way, the whole apparatus might be broken. Rest the potassa-apparatus upon a folded piece of cloth. Fig. 98 shows the whole arrangement.

e. To ascertain whether the joinings of the apparatus fit air-tight, put a piece of wood about the thickness of a finger (*s*), or a cork or other body of the kind, under the bulb *r* of the potassa-apparatus, so as to raise that bulb slightly (see Fig. 98). Heat the bulb *m*, by holding a piece of red-hot charcoal near it, until a certain amount of air is expelled through the apparatus; then remove the piece of wood (*s*), and allow the bulb *m* to cool. The solution of potassa will now rise into the bulb *m*, filling it more or less; if the liquid in *m* preserves, for the space of a few minutes, the same level which it has assumed after the perfect cooling of the bulb, the joinings may be considered perfect; should the fluid, on the other hand, gradually regain its original level in both limbs of the apparatus, this is a positive proof that the joinings are not air-tight. The few minutes which elapse between the two observations, may be advantageously employed in re-weighing the little tube in which the substance intended for analysis was originally weighed.

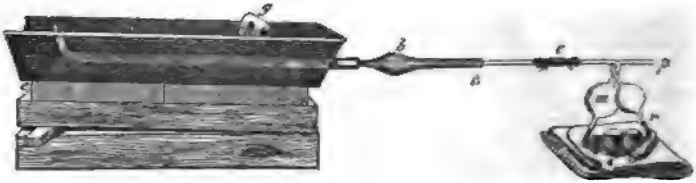

Fig. 98.

f. Arrange the position of the combustion tube in the furnace, so as to make the tube project a full inch beyond the latter; suspend the single screen over the anterior end of the furnace, as a protection to the cork; put the double screen over the combustion tube about two inches farther on (see Fig. 98), replace the little piece of wood (*s*) under *r*, and put small pieces of red-hot charcoal first under that portion of the tube which is separated by the screen; surround this portion gradually altogether with ignited charcoal, and let it get red-hot; then shift the screen an inch farther back, surround the newly exposed portion of the tube also with ignited charcoal, and let it get red-hot; shift the screen another inch farther back, surround with ignited charcoal, and proceed in this manner slowly and gradually extending the application of heat to the pointed end of the tube, taking care to wait always until the last exposed portion is red-hot before shifting the screen, and also to maintain the whole of the exposed portion of the tube before the screen in a state of ignition, and the projecting part of it so hot that the fingers can hardly bear the shortest contact with it. The whole process requires generally from ½ to 1 hour. It is quite superfluous, and even injudicious, to fan the charcoal during the operation;—this should be done only when the process is drawing to an end, as we shall immediately have occasion to notice.

The liquid in the potassa-apparatus is gradually displaced from the bulb *m* upon the application of heat to the anterior portions of the combustion tube, owing simply to the expansion of the heated air. When the heat reaches that portion of oxide of copper which has been used to rinse the mortar, a little carbonic acid and aqueous vapor are evolved, which drive out the whole of the air in the apparatus, and force it in large bubbles through the potassa-apparatus. The evolution of carbonic acid and aqueous vapor proceeds with greater briskness when the heat begins to reach the actual mixture; the first bubbles are only partly absorbed in the potassa-apparatus, as the carbonic acid contains still an admixture of air; but those which follow are so completely absorbed by the potassa, that a solitary air-bubble only escapes from time to time through the liquid. The process should be conducted in a manner to make the gas-bubbles follow each other at intervals of from ½ to 1 second. Fig. 99 shows the proper level of the solution of potassa, during the operation.

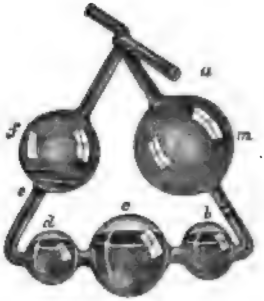

Fig. 99.

It will be seen from this that an air-bubble entering at *a* passes first into the bulb *b*, thence to *c*, from *c* to *d*, and passing over the solution in the latter, escapes finally into the bulb *f*, through the fluid which just covers the mouth of the tube *e*.

g. When the tube is in its whole length surrounded with red-hot charcoal, and the evolution of gas has relaxed, fan the burning charcoal gently with a piece of pasteboard. When the evolution of gas has entirely ceased, adjust the position of the potassa-apparatus to a level, remove the charcoal from the farther end of the tube, and place the screen before the point. The ensuing cooling of the tube on the one hand, and the absorption of the carbonic acid in the potassa-apparatus on the other, cause the solution of potassa in the latter to recede, slowly at first, but with increased rapidity from the moment the liquid reaches the bulb *m*. If you have taken care to adjust the position of the potassa-apparatus correctly, you need not fear that the contents of the latter will recede to the chloride of calcium tube. When the bulb *m* is about half filled with solution of potassa, break off the point of the combustion tube with a pair of pliers or scissors, whereupon the fluid in the potassa-apparatus will immediately resume its level. Restore the potassa-apparatus now again to its original oblique position, invert the glass tube mentioned § 174, 10, over the pointed end, supporting it against the arm of a filtering stand; join the suction-tube (§ 174, 9), or a caoutchouc-tube, to the potassa-apparatus, and apply suction until the last bubbles no longer diminish in size in passing through the latter.

Fig. 100 shows the arrangement of the apparatus at this juncture.

This terminates the analytical process. Disconnect the potassa-appa-

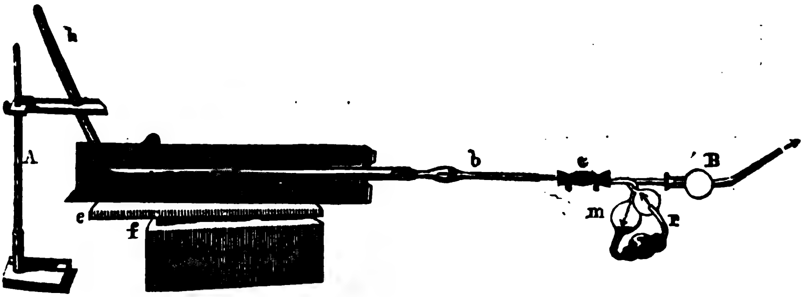

Fig. 100.

ratus and remove the chloride of calcium tube, together with the cork, which must not be charred, from the combustion tube; remove the cork also from the chloride of calcium tube, and place the latter upright, with the bulb upwards. After the lapse of half an hour, weigh the potassa-apparatus and the chloride of calcium tube, and then calculate the results obtained. They are generally very satisfactory;—as regards the *carbon*, they are nearly *absolutely* accurate, rather somewhat too low (about 0·1 per cent.) than too high. The method, indeed, is not altogether free from sources of error; but none of these interfere materially with the accuracy of the results, and the deficiency arising from the one is partially balanced by the excess arising from the other. In the first place, the air which passes through the solution of potassa during the combustion, and finally during the process of suction, carries away with it a minute amount of moisture. The loss arising from this cause is increased if the evolution of gas proceeds very briskly, since this tends to heat the solution of potassa; and also if nitrogen gas or oxygen gas passes through the potassa-apparatus (compare § 178 and § 183);—this may be remedied, however, by fixing to the exit end of the latter a weighed tube with solid hydrate of potassa. In the second place, traces of carbonic acid from the atmosphere are carried into the potassa-apparatus in the final process of suction; this may be remedied by connecting the pointed end of the combustion tube, during the operation, with a potassa tube, by means of a perforated cork. In the third place, it happens frequently, in the analysis of substances containing a considerable proportion of water or of hydrogen, that the carbonic acid is not absolutely dried in passing through the chloride of calcium tube; this may be remedied by fixing behind the chloride of calcium tube, a tube filled with asbestos moistened with sulphuric acid.

As regards the hydrogen, the results are somewhat too high, on an average about 0·1 to 0·15 per cent.; this arises principally from the circumstance that the air passing through the apparatus during the final process of suction conveys a little moisture into the chloride of calcium tube; but this may be readily remedied by connecting the pointed end of the combustion tube with a potassa tube.

I must, however, expressly remark that, in most cases, it is perfectly superfluous to make the operation more complicated for the purpose simply of correcting these defects, more particularly as we know from innumerable experiments the exact limits of the influence which they may exercise upon the accuracy of the results.

2. *Bunsen's Modification of Liebig's method* (*Kolbe*, "Handwörterbuch der Chemie," Supplemente, 186, *A. Strecker*, *Ibid.*, 2nd edition, I., 852).

§ 176.

The essential points of this modification are, that the oxide of copper is allowed to cool in a closed tube or flask, and that, instead of being mixed with the substance in a mortar, it is transferred at once to the combustion tube, and the operation of mixing effected in the latter, by which means the absorption of moisture from the air is effectually guarded against, and the application of the exhausting syringe dispensed with.

This modified process is more particularly suitable for the analysis of highly hygroscopic bodies and substances which cannot well be mixed with warm oxide of copper without risk of decomposition.

The dried substance is weighed in a tube of thin glass, about 20 centimetres long, and of about 7 centimetres diameter; one end of this tube is closed by fusion, the other, during the operation of weighing, with a small smooth cork.

Besides this weighing tube, *Bunsen's* method requires, like *Liebig's*, a combustion tube, potassa-apparatus, chloride of calcium tube, connecting tube of vulcanized india-rubber, perforated cork, suction tube, furnace, and oxide of copper (see § 174); and, in addition to these, a glass filiing tube, or flask (fig. 101), in which the freshly ignited oxide of copper is allowed to cool, and from which it is transferred to the combustion tube, secure from the possible absorption of moisture from the air.

The freshly ignited and still quite hot oxide of copper is transferred direct from the crucible to this filling tube, or flask, which is then closed air-tight with a cork. It saves time to fill in at once a sufficient quantity of oxide to last for several analyses. If the cork fits tight, the contents will remain several days fit for use, even though a portion has been taken out, and the tube repeatedly opened.

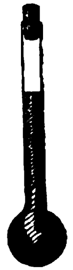

Fig. 101.

The filling of the combustion tube is effected as follows:—The perfectly dry tube is rinsed with some oxide of copper; a layer of oxide of copper, about 10 centimetres long, is introduced into the posterior end of the combustion tube, by inserting the latter into the filling tube or flask containing the oxide of copper (Fig. 102), holding both tubes in an oblique direction, and giving a few gentle taps.

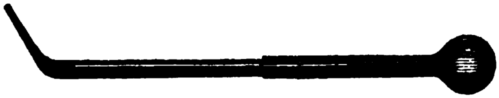

Fig. 102.

The tube with the substance intended for analysis has been accurately weighed shortly before, together with the cork. After removing the cork cautiously, to prevent the slightest loss of substance, the open end of the tube is inserted as deep as possible into the combustion tube, and the requisite quantity of substance poured from it, by giving it a few turns, pressing it all the while gently against the upper side of the combustion tube, to prevent its coming into contact with the powder already poured out; the two tubes are, in this manipulation, held inclined a little downwards (See Fig. 103).

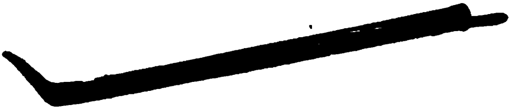

Fig. 103.

When a sufficient quantity of the substance intended for analysis has been thus transferred from the weighing to the combustion tube, the latter is restored to the horizontal position, which gives to the former a gentle inclination with the closed end downwards. If the little tube is now slowly withdrawn, with a few turns, the powder near the border of the opening falls back into it, leaving the opening free for the cork. The tube is then immediately corked and weighed, the combustion tube also being meanwhile kept closed with a cork. The difference between the two weighings shows the quantity of substance transferred from the weighing to the combustion tube. The latter is then again opened, and a quantity of oxide of copper, equal to the first, transferred to it from the filling tube, or flask, taking care to rinse down with this also the particles of the substance still adhering to the sides of the tube There are now in the hind part of the tube two layers of oxide of copper, each about ten centimetres long, and with the substance intended for analysis between them.

The next operation is the mixing; this is performed with the aid of a long clean iron wire, with a ring for a handle at one end, and pointed and twisted corkscrew fashion (with a single twist) at the other (see Fig. 104).

Fig. 104.

The wire is pushed down to the end, and rapidly moved about in all directions. A few minutes suffice to effect perfect intermixture; so perfect, indeed, in the case of pulverulent substances which do not cake, that the minutest particles can no longer be distinguished with the naked eye. The combustion is effected as in § 175.

β. Difficultly combustible non-volatile bodies, as, e. g., many resinous and extractive matters, coal, &c.

If substances of the kind are analysed by the methods given in §§ 175 and 176, minute particles of carbon are liable to escape combustion. To prevent this, one of the following methods is resorted to:—

1. COMBUSTION WITH CHROMATE OF LEAD, OR WITH CHROMATE OF LEAD AND BICHROMATE OF POTASSA.

§ 177.

Of the apparatus, &c., enumerated in § 174, only those marked from 1 to 12 are required, and in addition to these some chromate of lead (§ 66, 2). A narrow combustion tube may be selected, as chromate of lead contains a much larger amount of available oxygen in an equal volume than oxide of copper. A quantity of the chromate, more than sufficient to fill the combustion tube, is heated in a platinum or porcelain dish over a gas or Berzelius lamp, until it begins to turn brown; before filling it into the tube, it is allowed to cool down to 212° F.; and even below. The process is conducted as the one described in § 175, with the single difference that the application of the exhausting syringe is omitted, as chromate of lead is not hygroscopic like oxide of copper.

One of the principal advantages which chromate of lead has over oxide of copper as an oxidizing agent, being its property of fusing at a proper heat, the temperature must, in the last stage of the process of combustion, be raised (by fanning the charcoal, &c.) sufficiently high to fuse the contents of the tube completely as far as the layer of the substance extends. To heat the *anterior* end of the tube to the same degree of intensity would be injudicious, since the chromate of lead in that part would thereby lose all porosity, and thus also the power of effecting the combustion of the products of decomposition which may have escaped oxidation in the other parts of the tube.

As the chromate of lead, even in powder, is, on account of its density, by no means all that could be desired in this latter respect, it is preferable to fill the *anterior* part of the tube, instead of with chromate of lead, with coarsely pulverized oxide of copper, deprived of its hygroscopic properties by very intense ignition; or with copper turnings which have been superficially oxidized by ignition in a crucible with access of air.

In the case of very difficultly combustible substances—*e. g.*, graphites—it is desirable that the mass should not alone readily cake, but also, in the last stage of the process, give out a little more oxygen than is given out by chromate of lead. It is therefore advisable in such cases to add to the latter one-tenth of its weight of bichromate of potassa in powder (pulverized after previous fusion). With the aid of this addition, complete oxidation of even very difficultly combustible bodies may be effected (*Liebig*).*

2. COMBUSTION WITH OXIDE OF COPPER AND CHLORATE OR PERCHLORATE OF POTASSA.

§ 178.

This method requires the whole of the apparatus, &c., enumerated in § 174 or § 176, and in addition a small quantity of chlorate of potassa. The latter substance is freed from water by heating to the point of fusion, allowing to cool, and then reducing to coarse powder, which is kept in a warm place until required for use.

The process is conducted as in § 175 or § 176, with this difference, that the layer of oxide of copper in the posterior end of the tube is made about 5 centimetres long, instead of 3 or 4, and is mixed with about one-eighth (3 or 4 grms.) of chlorate of potassa; a layer of 2 centimetres of pure oxide of copper is placed between this mixture and that which contains the substance to be analysed. When, in the subsequent heating of the tube, you approach the part occupied by the mixture containing the chloride of potassa, do not fail to place the hot charcoal with the greatest caution, so as to ensure the very gradual decomposition of the chlorate; since, if you neglect this precaution, the impetuous rush of the gas will eject a small portion of the solution of potassa, thus vitiating the analysis altogether.

The oxygen liberated from the chlorate of potassa drives the carbonic acid before it, effects the combustion of the unconsumed particles of carbon, and oxidizes the reduced copper. Oxygen gas can therefore escape through the potassa-apparatus only when all that is oxidizable in the tube has been oxidized.

If in the last stage of the process of combustion, a large quantity of gas has in this way passed unabsorbed through the potassa-apparatus, it is unnecessary to break off the point, and draw air through the combustion tube, as the latter contains now only oxygen, and no longer carbonic acid nor aqueous vapour. But through the chloride of calcium tube and the potassa-apparatus, air* must be drawn, as these parts of the apparatus would otherwise be weighed full of oxygen.

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* *Mayer* has lately published a series of most successful experiments made with this excellent method ("Annal. d. Chem. u. Pharm.," 95, 204).

Chlorate of potassa decomposes with a certain degree of violence which is not the case with *perchlorate of potassa.* The latter salt, prepared by heating the former, may therefore be used instead of it, in the process of combustion, as *Bunsen* has proposed. The fused and still hot perchlorate is introduced into the farther end of the tube, a loose plug of recently ignited asbestos is inserted, and the tube then filled in the usual way. If *Bunsen's* mode of mixing (§ 176) is adopted, perchlorate must always be used in this method instead of chlorate of potassa.

As the dry oxygen gas passing through the potassa-apparatus carries away a little aqueous vapor from the solution of potassa, it is advisable to connect the exit tube of the apparatus by a cork, or a tube of vulcanized india-rubber, with a small tube filled with hydrate of potassa, which is afterwards weighed together with the potassa-apparatus; the increase of weight of the two is equal to the quantity of the carbonic acid absorbed.

3. Combustion with Oxide of Copper and Oxygen Gas.

§ 179.

Many chemists deviate, in the analysis of organic bodies, from the methods described in the preceding paragraphs, and effect the combustion with oxide of copper and oxygen gas, supplied by a gasometer. *Hess, Dumas* and *Stass, Erdmann* and *Marchand, Wöhler,* and others, have proposed methods based upon this principle, which they employ not only for the analysis of difficultly combustible bodies, but also to effect the determination of the carbon and hydrogen in organic substances in general.

As these methods require a gasometer filled with oxygen, also certain arrangements to dry the oxygen completely, and to free it from carbonic acid, it is evident that the apparatus must be more complicated than that of *Liebig,* or *Bunsen.* The application of these new methods is therefore generally resorted to in cases where a number of ultimate analyses have to be made in succession; and also more particularly in the analysis of substances which cannot be reduced to powder, and do not admit therefore of intimate mixture with the oxide of copper.

Hess, and *Erdmann* and *Marchand* use spirit of wine to heat the combustion tube. In English laboratories gas is frequently employed for the purpose;† or red-hot charcoal may be used, with the combustion furnace illustrated by fig. 93. Fig. 105 shows *Hess's* apparatus, with spirit of wine as the source of heat.

The nature of the fuel used as source of heat is without influence on the operation; the accuracy of the results also remains the same with the different sources of heat employed, provided, of course, that the heat may be regulated at will and carried to a proper degree of intensity.

a. In *Hess's* apparatus (Fig. 105), *aa* is a trough half filled with spirit of wine, which, in proportion as it burns, is replaced from the bottle *C,* through a tube opening below the level of the spirit of wine; *bb* are wick-holders made of tin, which contain broad flat wicks. They are nearly the breadth of the gutter of the trough, so that they may be moved to and fro in it. *dd* are screens, to confine the heat and promote the draught. The combustion tube, *cc*, lies in a small gutter of sheet iron, upon a layer of calcined magnesia.

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* Air dried and freed from carbonic acid answers the purpose best.

† See Hofmann's gas-furnace, page 448.

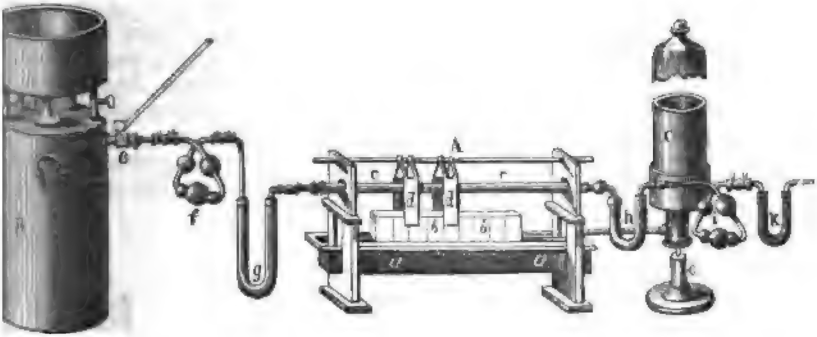

Fig. 105.

B is a gasometer with oxygen (§ 66, 4); the cock *e* is connected by a brass tube with the bulb apparatus *f*, which contains concentrated sulphuric acid. The handle of the cock is moved by means of a long lever, which greatly facilitates the opening and shutting. The brass tube is laterally connected, by means of a tube of vulcanized india-rubber, with a gasometer containing atmospheric air; this part of the apparatus is omitted in the engraving. The tube *g* contains solid hydrate of potassa; two or three tubes of the same description answer the purpose better than a single tube. *cc* represents the combustion tube, which is about 60 centimetres long, and open at both ends. This is connected, by means of perforated corks, at the posterior end with the potassa tube, at the anterior end with the chloride of calcium tube *h*: *i* is a potassa-apparatus; *k* contains solid hydrate of potassa.

The ignition of the oxide of copper is effected in the tube. To accomplish this, a tolerably dense stopper of copper turnings is inserted into the anterior end, the tube then filled to two-thirds of its length with oxide of copper; the posterior orifice is then joined to *g* and *f*, as shown in the drawing, and the tube heated to gentle redness in its whole length, whilst a slow current of atmospheric air is conducted through it. After complete ignition has been effected, the spirit of wine is extinguished, the anterior end of the combustion-tube, which has up to this time remained open, connected with a small chloride of calcium tube, and the ignited oxide allowed to cool in a slow stream of atmospheric air. When the tube is cold, it is opened at the posterior end, the substance introduced into it with the aid of a long tube (compare § 176), and quickly mixed with the oxide by means of an iron wire with twisted end (see Fig. 104); the after part of the tube is filled, to within about 12 centimetres, with ignited oxide of copper, cooled in the tube or flask shown in Fig. 101; a few gentle taps on the table will suffice to shake the contents down a little, leaving a clear passage above. The posterior end of the tube is then again connected with *g*, and the chloride of calcium tube, affixed to *b* during the cooling of the combustion tube, exchanged for the one marked h[*], which is accurately weighed first, and to which the weighed apparatus marked i and k are also joined.

The cock, e, of the oxygen gasometer is now opened a little, so that the gas may pass in a very slow current through the apparatus; the cock is then suddenly turned off, and the level of the fluid in the two bulb apparatus watched some time; if no change takes place in it, this is a proof that all the joinings fit air-tight. After this, the anterior portion of the tube is heated to redness, as far as the layer of pure oxide of copper extends; the same is then done with the farther part also, as far as the layer of pure oxide of copper extends, the corks at both ends of the tube being protected by screens, as well as also the part containing the mixture. A very slow current of oxygen gas is transmitted all the time through the apparatus.

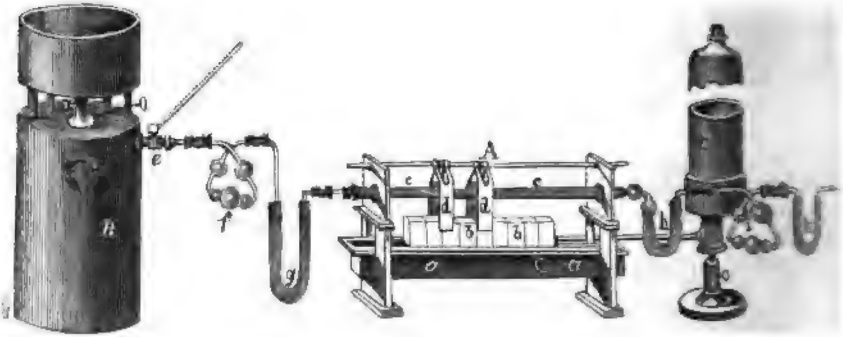

Fig. 106.

The part of the tube containing the mixture is then also heated, proceeding slowly from the anterior to the posterior part. The stream of oxygen gas is gradually increased, but never to an extent to allow the oxygen to escape through the potassa-apparatus, i. When the tube in its whole length is at a red heat, and the evolution of gas has ceased, the cock is opened a little wider, and the transmission of oxygen continued, until at last, when the reduced oxide of copper is completely re-oxidized, the gas begins to escape unabsorbed through the potassa-apparatus. The cock of the oxygen gasometer is now shut, whilst that of the air gasometer is opened a little; the ignited charcoal is removed as far as practicable, and the combustion-tube, &c., allowed to cool in a slow stream of atmospheric air. The chloride of calcium tube and the potassa-apparatus, with the potassa tube joined to it, are then weighed.

A very great advantage of this method consists in this, that the combustion tube, after the termination of the first, is quite ready for a second analysis.

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[*] Instead of drying the cork which connects h with the combustion tube, *Erdmann* and *Marchand* cover it with lead foil, in the following manner: the bottom of the cork is covered with a round piece of lead foil of the requisite size, and the projecting border part turned over and pressed firmly against the sides of the cork. The foil is then pierced at the part where it covers the perforation of the cork, by turning the narrow tube of the chloride of calcium apparatus cautiously into the latter from the bottom, then withdrawing it again, and turning it in from the top. In this way the tube is passed through, in most cases, without forcing off the lead foil.

b. The combustion of most substances may be effected also without mixing with oxide of copper, by introducing the sample into a platinum or porcelain boat (Fig. 107) which, at the same time, affords the advantage of enabling the operator to determine any residuary matter which may be left, as in the analysis of coal, for instance. The sample intended for analysis is weighed in the little boat, which is inserted into a small stoppered glass tube.

Fig. 107.

The process of combustion is then conducted as follows:—Introduce into the anterior end of the tube a plug of copper turnings, then fill the tube with oxide of copper, leaving about 20 centimetres free, and keep the oxide in its place by pushing an asbestos plug down upon it. Heat the tube now to redness, in the combustion furnace, pass a current of air through it, to remove all moisture, connect the anterior end with an unweighed chloride of calcium tube, and let the apparatus cool; then push the boat containing the sample down to the asbestos plug, and connect the after part of the tube with the potassa tube, &c., the fore part with the weighed chloride of calcium tube, potassa-apparatus and potassa-tube. Heat the oxide of copper in the combustion tube to redness, and when approaching the part where the boat is placed, open the cock of the oxygen gasometer a little; when the heat has reached the contents of the boat, proceed with proper caution, and take care to pass the proper quantity of oxygen through the tube. Increase the current of oxygen a little at last, and let the apparatus finally cool in a slow current of atmospheric air.

With this method, it is still easier than with *a* to use the combustion tube for a second analysis immediately after the first, as all required for the purpose is to insert a fresh boat with another sample of substance, to replace the one just removed.

This method has been employed with great success by *Wöhler*, *Piria*, *Hofmann*, *Strecker*, and others, and also in my laboratory.

γ. *Volatile Substances, or Bodies undergoing Alteration at* 212° F. (*losing Water, for instance*).

§ 180.

If substances of this kind were analysed as directed § 175, a portion of the substance or some water would escape upon mixing with hot oxide of copper and the application of the exhausting syringe to the tube, surrounded as it is with hot sand; the results, therefore, could not possibly be accurate. And if, on the other hand, the mixing were effected in the same way with *cold* oxide of copper, the mixture would absorb an appreciable quantity of water.

The process is therefore conducted either according to § 176, or as directed § 179. Ignited chromate of potassa, cooled in a closed tube, may also be employed as oxidizing agent.

b. LIQUID BODIES.

a. *Volatile liquids* (*e.g.*, ethereal oils, alcohol, &c.).

§ 181.

1. The analysis of organic volatile fluids requires all the objects enumerated in § 174, with the exception of the exhausting syringe and the apparatus for weighing and mixing; it requires besides a filling tube or flask, as described in § 176, for the temporary reception of the oxide of copper, and also several small glass bulbs for the reception of the liquid to be analysed. These bulbs are made in the following manner:

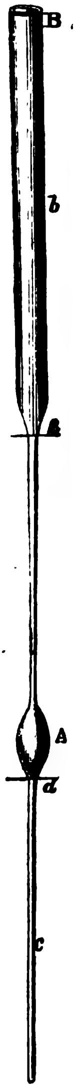

Fig. 108.

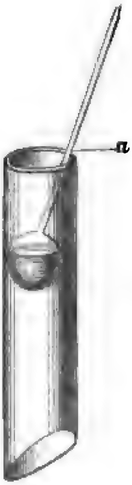

Fig. 110.

A glass tube, about 30 centimetres long and about 8 millimetres wide, is drawn out as shown in Fig. 108, cut off at *d*, in the blow-pipe flame, and A expanded into a bulb, as shown in Fig. 109. The bulbed part is then cut off at β. Another bulb is then made in the same way, and a third, and fourth, &c., as long as sufficient length of tube is left to secure the bulb from being reached by the moisture of the mouth.

Two of these bulbs are accurately weighed; they are then filled with the liquid to be analysed, closed by fusion, and weighed again. The filling is effected by slightly heating the bulb over a spirit-lamp and immersing the extreme end into the liquid to be analysed, part of which will now, upon cooling, enter the bulb. If the fluid is highly volatile, the portion entering the still warm bulb is converted into vapor, which expels the fluid again; but the moment the vapor is recondensed, the bulb fills the more completely. If the liquid is of a less volatile nature, a small portion only will enter at first; in such cases, the bulb is heated again to convert what has entered into vapor, and the point is then again immersed into the fluid, which will now readily enter and fill the bulb. The excess of fluid is ejected from the neck of the little tube by a sudden jerk; the open end of the capillary neck is then sealed in the blow-pipe flame. The combustion tube is now prepared for the process by introducing into it, from the filling-tube or flask (§ 176), a layer of oxide of copper occupying about 6 centimetres in length. The middle of the neck of one of the bulbs is slightly scratched with a file, the pointed end is quickly broken off, and the bulb and end are dropt into the combustion tube (See Fig. 110). Another layer of oxide of copper, about 6—9 centimetres long, is then filled in, and the other bulb introduced in the same manner as the first. The tube is finally nearly filled with oxide of copper. A few gentle taps upon the table suffice to clear a free passage for the gases evolved. It is advisable to place in the anterior part of the combustion tube small lumps of oxide of copper (compare § 166, 1), or superficially oxidized copper turnings, which will permit the free passage of the gases, even with a narrow channel; since with a wide channel, there is the risk of vapors passing unconsumed through the tube.

The combustion of highly volatile substances demands great care, and requires certain modifications of the common method. The operation commences by heating to redness the smaller anterior half of the tube, which is separated from the rest by a screen, or, in the case of highly volatile substances, by two screens; ignited charcoal is then placed behind the tube, to heat the pointed end, which prevents the condensation of vapor in that part. A piece of red-hot charcoal is now applied to that part of the tube which is occupied by the first bulb; this causes the efflux and evaporation of the contents of the latter; the vapor passing over the surface of the oxide of copper suffers combustion, and thus the evolution of gas commences, which is then maintained by heating very gradually the first, and after this the second bulb; it is better to conduct the operation too slowly than too quickly. Sudden heating of the bulbs would at once cause such an impetuous rush of gas as to eject the fluid from the potassa-apparatus. The tube is finally in its entire length surrounded with ignited charcoal, and the rest of the operation conducted in the usual way. If the air drawn through the apparatus tastes of the analysed substance, this is a sure sign that complete combustion has not been effected.

2. In the combustion of liquids of high boiling point and abounding in carbon, *e.g.*, ethereal oils, unconsumed carbon is apt to deposit on the completely reduced copper near the substance; it is therefore advisable to distribute the quantity intended for analysis (about 0·4 grm.) in 3 bulbs, separated from each other in the tube by interposed layers of oxide of copper.

3. In the combustion of less volatile liquids, it is advisable to empty the bulbs of their contents before the combustion begins, this is effected by connecting the filled tube with an exhausting syringe, and rarefying the air in the tube by a single pull of the syringe; this will suffice to expand the air-bubble in each bulb sufficiently to eject the oily liquid from it, which is then absorbed by the oxide of copper.

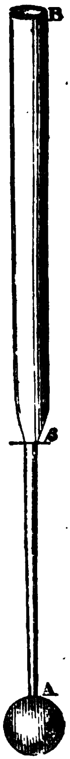

Fig. 109.

4. If there is reason to apprehend that the oxygen supplied by the oxide of copper may not suffice to effect the complete combustion of the carbon, the process is terminated in a stream of oxygen gas evolved from a layer of chlorate or perchlorate of potassa in the posterior part of the tube (compare § 178).

5. If it is intended to effect the combustion in the apparatus described in § 179, in a current of oxygen gas, the bulbs must be drawn out into a fine long point, and filled almost completely with the fluid. The point is then sealed in the blowpipe-flame, and the bulbs are transferred in that state to the combustion tube. When the anterior and the farther end of the tube are red-hot, a piece of ignited charcoal is put to the part occupied by the first bulb, when the expansion of the liquid will cause it to burst. When the contents of the first bulb are consumed, the second, and after this the third, are treated in the same way. This method will not answer however, for very volatile liquids, as *e.g.*, ether, on account of the explosion which would inevitably take place.

β. *Non-Volatile Liquids* (*e.g.*, fixed oils).

§ 182.

The combustion of non-volatile liquids is effected either, 1, with chromate of lead, or oxide of copper with chlorate or perchlorate of potassa; or, 2, in the apparatus described § 179.

1. The general operation is conducted as directed § 177 or § 178. The substance is weighed in a small tube, placed for that purpose in a tin foot (see Fig. 111), and the mixing effected as follows: Introduce into the combustion tube first a layer, about 6 centimetres long, of chromate of lead, or of oxide of copper and chlorate of potassa; then drop in the small cylinder with the substance, and let the oil completely run out into the tube; make it spread about in various directions, taking care, however, to leave the upper side (intended for the channel) and the forepart, to the extent of ¼ or ⅓ of the length of the tube, entirely clean. Fill the tube now nearly with chromate of lead or oxide of copper—which has previously been cooled in the filling tube—taking care that the little cylinder which contained the oil intended for analysis be completely filled with the oxidizing agent. Place the tube in hot sand, which, imparting a high degree of fluidity to the oil, leads to the perfect absorption of the latter by the oxidizing agent; apply the exhausting syringe, if necessary, and proceed with the combustion in the usual way. It is advisable to select a tolerably long tube. Chromate of lead is usually preferable as oxidizing agent to the mixture of oxide of copper and chlorate of potassa. If the former agent is used, a very intense heat, sufficiently strong to fuse the contents of the tube, is cautiously applied in the last stage of the process.

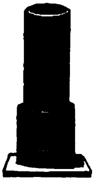
Fig. 111.

Solid fats or waxy substances which, not being reducible to powder, cannot be mixed with the oxidizing agent in the usual way, are treated in a similar manner to fixed oils. They are fused in a small weighed glass-boat (Fig. 112), made of a tube divided lengthwise; when cold, the little boat with its contents is weighed, and then dropped into the combustion tube, which has been previously filled to the extent of about 6 centimetres with chromate of lead, or with a mixture of oxide of copper and chlorate of potassa. The substance is then fused by the application of heat, and made to spread about in the tube in the same manner as is done with fixed oils; the rest of the operation also being conducted exactly as in the latter case. If chromate of lead is employed as oxidizing agent, it will be found advantageous to add some bichromate of potassa.

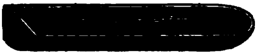
Fig. 112.

2. If it is intended to effect the combustion of fatty substances or other bodies of the kind, in a current of oxygen gas, in the apparatus described in § 179, the substance is weighed in a glass or porcelain-boat, which is then inserted into the tube, and the posterior part of the latter filled with oxide of copper as directed above. The combustion must be conducted with great care. As soon as the oxide of copper in the anterior and the posterior parts of the tube is red hot, a piece of red hot charcoal is put to the part occupied by the little boat. The volatile products generated by the dry distillation of the substance burn at the expense of the oxygen of the oxide of copper.

When it is perceived that the surface layer of the oxide of copper is reduced to the metallic state, the application of heat is suspended for a time, and resumed only after the reduced copper is re-oxidized in the stream of oxygen gas. Care is finally taken to insure the complete combustion of the carbon remaining in the boat.

B. ANALYSIS OF COMPOUNDS CONSISTING OF CARBON, HYDROGEN, OXYGEN AND NITROGEN.

The principle of the analysis of such compounds is in general this: the substance is divided into two portions, and the carbon determined as carbonic acid, the hydrogen as water, in *one* portion; the nitrogen in the *other* portion, either in the gaseous form, or as chloride of ammonium and bichloride of platinum, or by neutralizing the ammonia formed by the liberated nitrogen; the oxygen is calculated from the loss.

As the presence of nitrogen exercises a certain influence upon the quantitative estimation of carbon and hydrogen, we have to consider not only the method of determining the nitrogen in organic compounds, but also the modifications which the presence of the nitrogen renders necessary in the usual method of determining the carbon and hydrogen.

a. DETERMINATION OF THE CARBON AND HYDROGEN IN NITROGENOUS SUBSTANCES.

§ 183.

1. When nitrogenous substances are ignited with oxide of copper or with chromate of lead, a portion of the nitrogen present escapes in the gaseous form, together with the carbonic acid and aqueous vapor; whilst another portion, minute indeed, still, in bodies abounding in oxygen, not quite insignificant, is converted into nitric oxide gas, which is subsequently transformed wholly or partially into nitrous acid by the air in the apparatus. The application of the methods described in § 175, &c., in the analysis of nitrogenous substances would accordingly give a higher number for the carbon than corresponds to the actual amount of that element present in the analysed substance; since the solution of potassa in the apparatus would retain, besides the carbonic acid, also the nitrous acid formed and a portion of the nitric oxide (which in the presence of potassa decomposes slowly into nitrous acid and nitrous oxide). This defect may be remedied, on the one hand, by the exclusive use of oxide of copper as oxidizing agent, the most intimate mixture of the substance with the oxide, and slow combustion; as brisk combustion and the use of chromate of lead, or the addition of chlorate of potassa to the oxide of copper, tend greatly to promote the evolution of nitric oxide; and, on the other hand, by selecting a combustion tube about 12—15 centimetres longer that those commonly employed, filling this in the usual way, but finishing with a loose layer, about 9—12 centimetres long, of clean fine copper turnings (§ 66, 7). The process is commenced by heating these copper turnings to redness, in which state they are maintained during the whole course of the operation. These are the only modifications required to adapt the methods given in § 175, &c., for the analysis of nitrogenous substances. The action of the copper turnings in the process rests upon the property of metallic copper in a state of intense ignition to decompose all the oxides of nitrogen into oxygen,

with which the metal combines to oxide, and into pure nitrogen gas. As the metal exercises this action only when in a state of intense ignition, care must be taken to maintain the anterior part of the tube in that state throughout the process. As metallic copper recently reduced retains hydrogen gas, and, when kept for some time, aqueous vapor condensed on the surface, the copper turnings intended for the process must be introduced into the tube hot as they come from the drying closet (which is heated to 212° F.). *Liebig* recommends to compress the hot turnings in a tube into a cylindrical form, to facilitate their introduction into the combustion tube.

2. If it is intended to burn nitrogenous bodies in the apparatus described in § 179, the combustion tube should be about 75 centimetres long, and the anterior part of it filled with a layer, 9—12 centimetres long, of clean copper turnings. Care must be taken to keep at least the anterior portion of the turnings from oxidizing both during the ignition in the current of air and during the actual process of combustion. When the operation is terminated, and the oxidation of the metallic copper is visibly progressing, the oxygen is turned off, and the cock of the air gasometer opened a little instead, to let the tube cool in a slow stream of atmospheric air.

b. DETERMINATION OF THE NITROGEN IN ORGANIC COMPOUNDS.—It has already been stated above that two essentially different methods are pursued to effect the determination of the nitrogen in organic compounds; viz., the nitrogen is either separated in the gaseous form and determined by measuring the volume of the isolated gas; or it is converted into ammonia, which again is then determined either as bichloride of platinum and chloride of ammonium, or by neutralization.

a. Determination of the Nitrogen from the Volume.

The many methods that have been recommended to effect this purpose, may all be brought under two general heads; viz., 1st, methods having for their object the collection of the whole of the nitrogen contained in a weighed portion of the substance; and 2nd, methods determining simply the relative proportion between the carbonic acid and the nitrogen gas evolved, from which the quantity of the nitrogen is then calculated; these latter methods require therefore, of course, that the amount of carbon contained in the substance should be previously known. The methods based upon the former principle are denominated *absolute* or *quantitative*, those based upon the latter are called *relative* or *qualitative*. I select here of each class those which are most readily performed and give the most accurate results.

I. RELATIVE DETERMINATION OF NITROGEN BY VOLUME.

§ 184.

aa. Liebig's method (Liebig's "Hand-book of Organic Analysis," edited by *A. W. Hofmann*, page 61).

This method is suitable only for the analysis of substances containing a not too inconsiderable amount of nitrogen in proportion to that of the carbon. See also the end of this paragraph.

The process requires 6—8 accurately graduated tubes of strong glass, each about 30 centimetres long and 15 millimetres in diameter; also a tall cylinder of strong glass, widened at the top (see Fig. 114).

The process is conducted in the following manner: A quantity of oxide of copper sufficient to form a layer of 6 centimetres in length, is introduced into the farther end of the combustion tube, which should be 60 centimetres long, and sealed at the posterior end; a quantity of about 0·5 grm.* of the very finely pulverized substance intended for analysis is then most intimately mixed with a portion of oxide of copper sufficient to fill the combustion tube about half. This mixture is introduced into the tube and followed by another layer of oxide of copper; the rest of the tube—a part at least 12 centimetres long—is then filled with copper turnings. The combustion tube so prepared is connected with the delivery tube, and placed in the furnace; the anterior part of the tube is then surrounded with red-hot charcoal, the part occupied by the mixture being protected by a screen which is shifted back 3 centimetres each time, as the application of heat is gradually advanced in the usual way towards this part. When about one-fourth of the mixture is decomposed, and the atmospheric air is thus almost completely expelled from the tube by the products of the combustion, one of the graduated tubes, filled with mercury,† is inverted over the mouth of the bent delivery-tube, which opens under mercury, and allowed to fill with gas to about ⅘; it is then lifted out of the mercurial trough, so that the rest of the mercury flows out; if, upon looking through the tube lengthwise, the operator perceives not the slightest red coloration of the gaseous contents, he may feel convinced that the gases contain no admixture of nitric oxide. To acquire the positive certainty that there is no nitric oxide in any of the tubes, this must be repeated about the middle and towards the end of the operation. After this preliminary experiment, the graduated tubes are filled one after another in the same way (see Fig. 113), whilst the heating is continued slowly and uniformly.

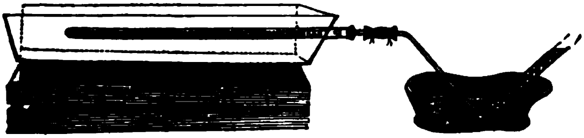

Fig. 113.

This operation requires a stand with places for six or eight tubes.‡ In default of an apparatus of the kind, an assistant must hold the filled tubes until they are required for measuring; care must be taken to mark the order in which they were filled. The anterior part of the tube must be kept at a bright red heat throughout the operation.

When all the tubes are filled, the gas is measured successively in them in the following manner. The tube is completely immersed for some time in the mercury with which the cylinder (Fig. 114) is filled; by this means perfect uniformity of temperature between the gas and the mercury is established. After this, the tube is raised until the mercury inside and outside is on an exact level; the volume is then read off and noted (see § 13). A small quantity of solution of potassa is now made to pass into the tube from the pipette β, which is nearly filled with this liquid; this is effected by blowing cautiously into the pipette. The latter is then withdrawn, and the absorption of the carbonic acid by the solution of potassa promoted by moving the firmly held tube up and down in the mercury, pressing its mouth firmly against the side of the cylinder; the tube is ultimately once more completely immersed, raised again until the mercury inside and outside is on an exact level, and the volume then accurately read off. The pressure which the small column of solution of potassa exercises may be altogether disregarded. The volume of the carbonic acid is determined by subtracting the quantity found in the second measuring (the nitrogen gas), from that noted in the first (nitrogen gas + carbonic acid gas).

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* The weight need not be more accurately known in this process.

† The best way of filling a tube completely with mercury, so as to prevent any air-bubbles remaining in it, is to pour in the mercury through a funnel tube reaching down to the bottom of the graduated tube, then close the aperture with the finger, invert the tube, and make the minute bubbles of air adhering to the sides gradually unite with the large bubble at the top. The tube is then turned upright, and slowly filled up with mercury.

‡ Compare "Das Chemische Laboratorium zu Giessen," von *J. P. Hofmann*, Heidelberg, 1842.

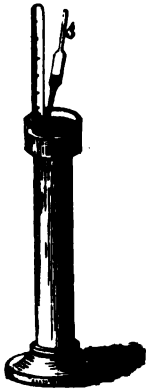

Fig. 114.

When the contents of the first tube have thus been determined, the mercury is cleaned by washing first with water slightly acidulated with hydrochloric acid, then with pure water, and drying with blotting paper; the contents of the second tube are then determined in the same manner, and so on to the last.

The results of the several tubes are generally found pretty uniform; in many cases, however, where the nitrogenous substance is, previous to complete combustion, resolved into products of different degrees of volatility, the several tubes show notable differences in the respective results. As a general rule, the arithmetical mean is taken as correct, and this may be considered the more accurate and reliable, the less the respective results of the several tubes diverge from it. If, however, the tubes first filled give a considerably larger proportion of nitrogen than those filled after, it may be safely assumed that the air was not completely expelled when the first tubes were filled; and in that case their contents are not taken into account.

The relative proportion of the carbonic acid to the nitrogen gas expresses directly, and without further calculation, the proportion which the equivalents of the carbon bear to those of the nitrogen: since 1 equivalent of carbon combines with 2 equivalents of oxygen, leaving the volume of the latter element unaltered, and giving accordingly 2 volumes of carbonic acid;—and 1 equivalent of nitrogen gives equally 2 volumes of nitrogen gas.

Suppose we have found the proportion which the carbonic acid bears to the nitrogen gas as $4 : 1$, the analysed compound contains, in that case, to 4 equivalents of carbon $= 4 \times 6 = 24$, 1 equivalent of nitrogen $= 14$. If, therefore, we have found 26 parts of carbon in 100 parts of the analysed substance, the latter contains 15·17 of nitrogen; since $24 : 14 :: 26 : x$; $x = 15{\cdot}17$.

There is one irremediable source of error inherent in this method, viz., it is impossible to remove the air completely from the tube, and thus the resulting number for the nitrogen is somewhat too high. This defect, however, does not materially interfere with the correctness of the results, if the substance contains a relatively large amount of nitrogen; thus, for instance, if the proportion found is as 1 : 4·1, it is at once evident that 1 : 4 is the correct number. But if the relative proportion of the nitrogen is inconsiderable, this defect vitiates the results; and experience has proved that the method is not suitable for the analysis of substances containing less than 1 equivalent of nitrogen to 8 equivalents of carbon.

bb. Bunsen's Method (see *Kolbe's* paper on the subject in the "Handwörterbuch der Chemie," supplement to 1st edition, page 200).

The results are more accurate than those attainable by *aa*, but the method is less simple and demands greater dexterity and expertness. The process is conducted as follows:—

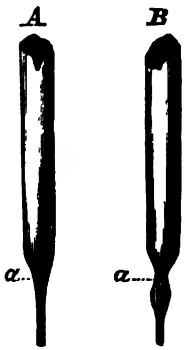

Fig. 115.

In the first place, select a tube of strong, difficultly fusible glass, about 38 centimetres long, and 2 centimetres wide; draw this out at one end as shown in Fig. 115, A, then narrow the part marked *a*, as shown in Fig. 115, B. This latter manipulation is necessary to give the tube the requisite power of resistance against the internal pressure exerted upon it by the gas evolved during the process of ignition. The drawn-out part must, moreover, altogether remain stout.

Clean the tube, then introduce into it an intimate mixture of about 5 grammes of loose ignited oxide of copper with 3—5 centigrammes of the substance (which, however, need not be accurately weighed), together with a small quantity of clean copper turnings (§ 66, 7). Draw out the other end, at a distance of 17—20 centimetres from the narrowed part, in the same way as above. Volatile liquid bodies are introduced into the tube, best in a capillary tube, sealed at one or both ends.

Connect the tube now, as shown in Fig. 116, at one end with a globe,

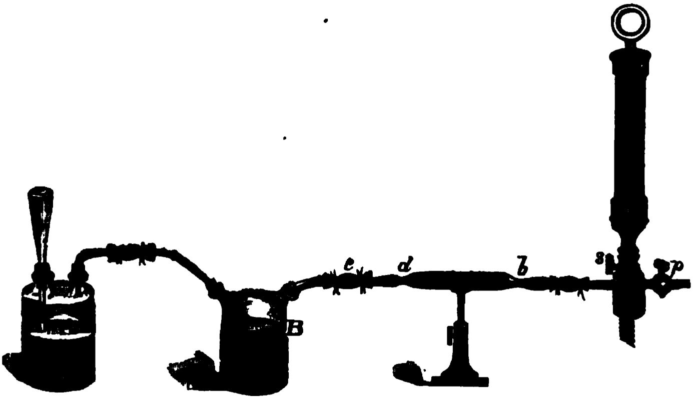

Fig. 116.

B, half filled with sulphuric acid, in which the hydrogen gas evolved from A is dried, at the other end with an exhausting syringe, with the cock, *p*, open, to let the hydrogen gas escape.

When the hydrogen gas has passed through the apparatus long enough to ensure the complete expulsion of the air, turn off the cock *p*, open A, compress *c*, by a clamp, draw up the piston of the exhausting syringe with a quick motion, and then immediately turn off the cock *s*. This serves to rarefy the hydrogen gas in the tube, and you may now divide and seal the latter at *d*, in the blow-pipe flame, without risk of swelling. Now exhaust as completely as possible, and then cut off and seal the tube also at *b*.

If the tube so prepared were exposed to a red heat in the usual way, the pressure exerted upon it from within by the evolved gas would inevitably expand it; to avoid this, it is enclosed in a mould made of strong sheet iron (Fig. 117).

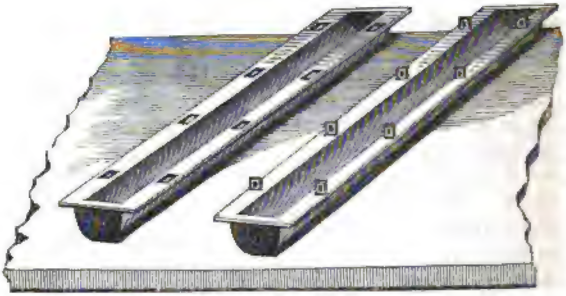

Fig. 117.

The two parts fit accurately upon each other, enclosing a cylindrical hollow, 30 centimetres long, and 5—6 centimetres in diameter. They are both filled with freshly prepared gypsum paste, mixed with a handful of cow-hair cut small; the combustion tube is pressed into the one half, in the middle, and as soon as the paste is beginning to set, the other half pressed down upon it, and the mould closed by small iron wedges (see Fig. 118).

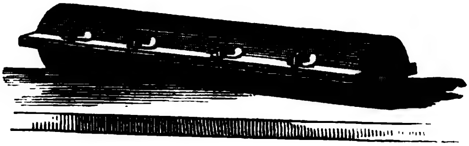

Fig. 118.

There are 10 or 12 holes in the bulging part of each half, to give free issue to the aqueous vapors, &c.

After the gypsum has thoroughly set, heat the mould in a suitable furnace, slowly, to dull redness. As soon as the smell of burnt hair diminishes, and the mould, entirely surrounded with red-hot charcoal, is at a bright red heat, cover the coals with ashes, and continue heating in this way for another half-hour. After cooling, take the tube out of the mould with proper care; it should look dull and opaque, and show a blistered surface, as a proof that it has been thoroughly softened in the process. If too large a quantity of substance has been used, or the heat carried to a very high degree of intensity, the tube will occasionally present an expansion in some part. Break off the point under mercury, so as to receive the gaseous contents in a graduated tube filled with mercury (§ 12), into which a drop of water has been introduced (§ 16). This serves to saturate the moist gas with aqueous vapor. Though it is not necessary to transfer the whole of the gas from the combustion tube to the graduated tube, still the volume should be sufficiently large for the purpose of the analysis which is to follow.

Note now the state of the barometer and thermometer, and the height of the mercurial column in the graduated tube; then introduce a moistened ball of hydrate of potassa, fused on to an iron or platinum wire, which will absorb the carbonic acid gas. Dry the residual nitrogen gas by introducing a second unmoistened ball of hydrate of potassa, then measure. Reduce the volumes to the same temperature and pressure, and to the same state of dryness; this will give you the relative proportion of the volumes of the carbonic acid and of the nitrogen, and accordingly also that of the equivalents of the carbon and nitrogen in the analysed substance.

cc. Marchand's Method ("Journ. f. prakt. Chem.," 41, 177), modified by *Gottlieb* ("Annal. d. Chem. u. Pharm.," 78, 241).

Draw the posterior end of a long combustion tube out to an open point; introduce first an asbestos plug, then the mixture of 0·1—0·12 grms. of the substance with a large quantity of oxide of copper, then a layer of pure oxide of copper, 6 centimetres long, a layer of copper turnings 12—14 centimetres long, and lastly, a layer 6 centimetres long, of coarsely powdered fused chloride of calcium. Connect the anterior end of the tube with a delivery tube bent at a right angle, the descending limb of which is 80 centimetres long, and transmit dried hydrogen gas for two hours through the apparatus; towards the end of the operation the delivery tube must dip under the mercury in the trough. Seal the tube now at the posterior end, heat the pure oxide of copper (the oxygen of which will combine with the hydrogen, thus creating a vacuum), invert over the end of the delivery tube a graduated tube filled with mercury, and then proceed to combustion. The process will give 90—100 cubic centimetres of gas, of which about half may be used for analysis, the remainder to test for nitric oxide gas. *Gottlieb* obtained very satisfactory results by this method.*

dd. For *Simpson's* method of effecting the combustion with a mixture of oxide of copper and oxide of mercury, I refer to the paper on that subject in "Annal. d. Chem. u. Pharm.," 95, 64.

II. ABSOLUTE DETERMINATION OF NITROGEN BY VOLUME.

§ 185.

a. Dumas' Methods.

This method may be employed in the analysis of all organic compounds containing nitrogen. It requires a graduated glass cylinder of about 200 c.c. capacity, with a ground-glass plate to cover it.

The combustion tube should be about 70 or 80 centimetres long, and sealed at the posterior end by fusion, in the manner of a test tube. Introduce into it a layer of pure dry bicarbonate of soda, 12—15 centimetres long, then a layer of oxide of copper, 4 centimetres long; after this the intimate mixture of an accurately weighed portion of the substance (0·300—0·600 grm., or, in the case of compounds poor in nitrogen, a somewhat larger quantity), with oxide of copper, then the oxide which has served to rinse the mortar, followed by a layer of pure oxide, and lastly a layer of copper turnings, about 15 centimetres long.* Connect the tube so prepared with the bent delivery tube *cf* (see Fig. 119), and place in the the furnace. Heat the posterior end of the tube (to the extent of about 6 centimetres) gradually to redness, protecting the other parts by a screen. The bicarbonate of soda is decomposed by the heat, and the carbonic acid evolved drives the air in the tube before it, thus effecting its expulsion. When the evolution of gas has proceeded for some time, immerse the end of the bent delivery tube under mercury, invert over it a test cylinder filled with solution of potassa, and advance the red-hot pieces of charcoal a little towards the anterior part of the tube. If the gas bubbles entering the cylinder are completely absorbed by the solution of potassa, this is a proof that the air is thoroughly expelled from the tube; the actual combustion may therefore now be at once commenced. But should this not be the case, the evolution of carbonic acid must be continued until the desired point is attained. Invert the graduated cylinder, filled $\frac{2}{3}$ with mercury, $\frac{1}{3}$ with concentrated solution of potassa, over the end of the delivery tube, with the aid of the ground-glass plate,† and proceed with the combustion in the usual way, heating first the anterior part of the tube to redness, and advancing gradually towards the farther end. In the last stage of the process, the other half of the bicarbonate of soda is decomposed, and thus the whole of the nitrogen gas which still remains in the tube is forced into the cylinder. Wait now until the volume of the gas in the cylinder no longer decreases, even upon shaking the latter (consequently, until the whole of the carbonic acid has been absorbed). Then place the cylinder in a large and

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* *Heintz's* absolute method of determining nitrogen is based upon the same principle ("Journ. f. prakt. Chem.," 55, 229).

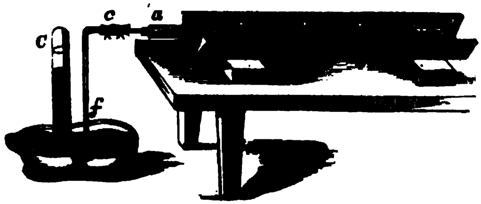

Fig. 119.

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* *Melsens* ("Annal. d. Chem. u. Pharm." 60, 115) recommends tubes of a length of 1·10 to 1·25 metre, which he fills as follows: bicarbonate of soda, 16 centimetres, coarse oxide of copper, 20 centimetres; the substance, triturated with fine oxide, then mixed with coarser oxide of copper, 30 centimetres; coarse oxide, 30 centimetres; metallic copper, 20 centimetres.

† The following is the best way of filling the cylinder and inverting it over the opening of the bent delivery tube. The mercury is introduced first, and the air-bubbles which adhere to the walls of the vessel are removed in the usual way. The solution of potassa is then poured in, leaving the top of the cylinder free, to the extent of about 2 lines; this is cautiously filled up to the brim with pure water, and the ground-glass plate placed over it. The cylinder is now inverted, and the opening placed under the mercury in the trough; the glass plate is then withdrawn from under the cylinder. In this manner the operation may be performed easily, and without soiling the hands with the solution of potassa.

deep glass vessel, filled with water, the safe transport from the mercurial trough to this vessel being effected by keeping the aperture closed with a small dish filled with mercury. The mercury and the solution of potassa sink to the bottom, and are replaced by water. Immerse the cylinder, then raise it again until the water is inside and outside on an exact level; read off the volume of the gas, and mark the temperature of the water, and the state of the barometer; calculate the weight of the nitrogen gas from its volume, after previous reduction to 32° F. of the thermometer, and 29·8 of the barometer, and with due regard to the tension of the aqueous vapor (compare "Calculation of Analyses"). The results are generally somewhat too high, viz., by about 0·2—0·5 per cent.; this is owing to the circumstance that even long-continued transmission of carbonic acid through the tube fails to expel every trace of atmospheric air adhering to the oxide of copper.

To ensure complete combustion of difficultly combustible bodies, *Strecker* ("Handwörterbuch der Chemie," 2nd edit. I., 878) recommends the addition of arsenious acid in powder to the oxide of copper with which the substance is to be mixed; the arsenious acid is volatilized by the action of the heat, the fumes burning the whole of the carbon like a current of oxygen. The arsenious acid sublimes in the anterior part of the tube, arsenic remains with the copper.

b. Simpson's method ("Annal. d. Chem. u. Pharm.," 95, 74).

The *principle* of this method, which is well suited for the analysis of all nitrogenous bodies, and gives accurate results also in the case of difficultly combustible organic compounds, is the same as that upon which *Dumas'* method (*a*) is based; but the *process* differs in some essential points. The carbonic acid which serves to expel the air from the tube is evolved from carbonate of protoxide of manganese; the combustion is effected at the expense of a mixture of oxide of mercury with oxide of copper; the free oxygen gas is absorbed by copper in a state of ignition; the gaseous mixture is received in a special apparatus, in which the carbonic acid is removed by solution of potassa, the nitrogen gas being then transferred to a graduated tube, and finally measured over mercury.

Select a strong combustion tube, about 80 centimetres long, and seal one end in the blow-pipe flame. Then introduce a mixture of 12 grammes of carbonate of protoxide of manganese, dried at 212° F., and 2 grammes of oxide of mercury.* Push down a plug of recently ignited asbestos, leaving an inch clear space between it and the mixture, so as to admit of the formation of a sufficiently wide free passage for the evolved gas when the tube is placed in a horizontal position. Then introduce 1 grm. of oxide of mercury. Mix the accurately weighed substance (about 0·5 or 0·6 grm.) with 45 times the weight of previously prepared and dried mixture of 4 parts of recently ignited oxide of copper and 5 parts of oxide of mercury, and transfer the mixture, without loss, to the combustion-tube, rinsing the mortar with some pure oxide of copper and some mixture of oxide of copper and oxide of mercury, and transferring the rinsings also to the combustion tube. Push down another asbestos plug, which should be about 30 centimetres distant from the first, and considering that a free passage of ample width should be left clear above the mixture, when the tube is placed in a horizontal position; bear in mind also, that the plug is partly intended to clear the part of the tube through which it passes, of the particles of the mixture adhering to the sides. Introduce now a layer, 6—9 centimetres long, of pure oxide of copper, then a third asbestos plug, and finally a layer, 20—24 centimetres long, of metallic copper, prepared by reducing granular oxide of copper in a current of hydrogen gas.* Draw out the anterior end of the tube, and connect it, by means of a small caoutchouc tube, with a delivery tube, bent at a right angle, which dips in the mercurial trough.

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* This addition of oxide of mercury is intended to effectively guard against the possibility of the formation of carbonic oxide gas, which might otherwise be apprehended from accidental presence of organic matter.

Place the tube in the combustion-furnace, after having, by a few gentle taps, cleared a free passage for the evolved gases from end to end. Now prepare the apparatus for the reception of the gaseous mixture (Fig. 120).

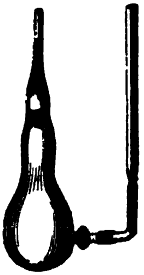

Fig. 120.

This should be made of strong glass, and hold about 200 c.c.; the upper part should have an outer diameter of 7—8 millimetres. Push a strong vulcanized india-rubber tube, 5 centimetres long, over the extreme end of the vessel, leaving about 3 centimetres of tubing projecting beyond; tie securely with silk cord, insert into the projecting end a solid glass rod, ground at both ends, 15 millimetres long, and of the same diameter as the india-rubber tube, and push this down until it touches the extreme end of the vessel; then insert into the upper part of the caoutchouc tube still left free, a very narrow gas delivery tube of the same diameter as the glass rod; tie this also securely, and then tie silk cord round the portion occupied by the glass rod. This is intended to close the vessel air-tight. Ascertain whether you have fully succeeded in this, by inverting the vessel, partly filled with mercury, under mercury, and observing whether the mercury will fall. If this experiment shows the joinings to be perfectly air-tight, fill the apparatus to the top with mercury and 16—17 c.c. of concentrated solution of potassa, invert it in the trough, and secure it in the manner shown in Fig. 121.

Separate the posterior half of the layer of carbonate of protoxide of manganese by a screen, heat the separated portion a few minutes with red-hot charcoal, until the disengaged carbonic acid has expelled the air from this part of the tube; then remove the charcoal, and heat by degrees the other half of the carbonate of protoxide of manganese, before the screen, to redness, as well as also the copper and oxide of copper in the anterior part of the tube, protecting by screens the portion occupied by the mixture. As soon as the evolution of carbonic acid ceases, insert the end of the gas delivery tube, without lifting it above the mercury, under which it has been kept submerged from the beginning, into the orifice of the gas apparatus; then heat the mixture, proceeding slowly from the anterior to the farther end. The fore part of the tube and the part occupied by the exhausted portion of the manganese salt must both be kept in a state of ignition during the whole process of combustion.

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* As regards the modifications in the process of filling, in the analysis of liquids, I refer to the original paper ("Annal. d. Chem. u. Pharm.," 95, p. 83).

When complete combustion of the mixture has been effected, decompose also the manganese salt behind the screen ; the carbonic acid evolved will force the whole of the nitrogen gas into the receiver. As soon as the gas bubbles are completely absorbed by the potassa solution, the gas delivery tube may be removed.

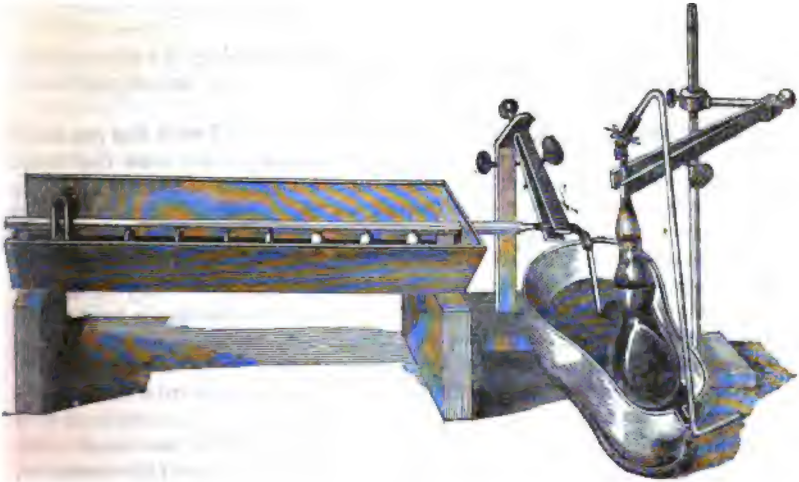

Fig. 121.

To transfer the nitrogen collected in the apparatus to a graduated tube for measuring, insert a tube of the form shown in Fig. 120, by means of a well-fitting perforated cork, under the mercury, into the tubulature of the gas vessel, taking care to moisten the cork previously

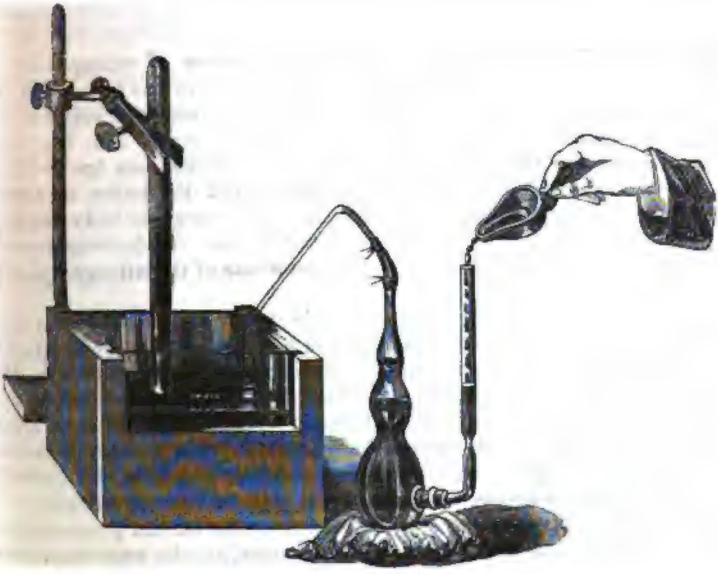

Fig. 122.

with solution of chloride of mercury, to guard against the possible introduction of air into the gas vessel. Pour mercury into the tube until it reaches a considerably higher level than in the gas vessel, and allow the whole to stand for two hours, to give time for the complete absorption of the carbonic acid.

Meanwhile fill the graduated tube for measuring the nitrogen gas, with mercury, having previously introduced a drop of water, and invert it in the trough.

Introduce the point of the delivery tube connected with the gas vessel into the opening of the measuring tube, take off the silk cord tied round the portion of the caoutchouc tube occupied by the glass rod, and pour mercury into the upright tube (see Fig. 122).

When the gas has in this manner been almost completely forced over into the measuring tube, add the mercury only drop by drop, until the potassa just begins to make its appearance in the gas delivery tube. By this course of proceeding, exactly as much nitrogen gas is kept out of the measuring tube, as air has at first entered (from the delivery tube). Care must be taken in pouring in the mercury, that no air finds its way into the measuring tube; to this end, the upright tube should from the first be poured pretty full, and the glass rod in the caoutchouc tube be selected of sufficient thickness to oppose considerable resistance to the passage of the gas. Note the state of the barometer and thermometer, measure the moist gas, and calculate the weight from the volume. *Simpson* obtained very satisfactory results by this method, in the analysis of vegeto-alkalies, nitrate of potassa, and chloride of ammonium.

β. *Determination of Nitrogen by Weight.*

Varrentrapp and Will's Method.

§ 186.

This method may be employed for the estimation of nitrogen in all nitrogenous compounds, except those containing it in the form of nitric acid, hyponitric acid, &c. It is based upon the same principle as the method of examining organic compounds for nitrogen (§ 172, 1, *a*), viz., upon the circumstance that, when nitrogenous bodies are ignited with the hydrate of an alkali, the water of hydration of the latter is decomposed, the oxygen forming with the carbon of the organic body carbonic acid, which then combines with the alkali, whilst the hydrogen at the moment of its liberation combines with the whole of the nitrogen present to ammonia.

In the case of substances abounding in nitrogen, such as uric acid, mellone, &c., the whole of the nitrogen is not at once converted into ammonia in this process; a portion of it combining with part of the carbon of the organic matter to cyanogen, which then combines, either in that form with the alkali metal, or in form of cyanic acid with the alkali. Direct experiments have proved, however, that even in such cases the whole of the nitrogen is ultimately obtained as ammonia, if the hydrated alkali is present in excess, and the heat applied sufficiently intense.

As in all organic nitrogenous compounds the carbon preponderates over the nitrogen, the oxidation of the former, at the expense of the water, will invariably liberate a quantity of hydrogen more than sufficient to convert the whole of the nitrogen present into ammonia; for instance,

$$C_2N + 4\,HO = 2\,CO_2 + NH_3 + H.$$

The excess of the liberated hydrogen escapes either in the free state, or in combination with the not yet oxidized carbon, according to the relative proportions of the two elements and the temperature, as marsh gas or olefiant gas, or as vapor of readily condensible carbides of hydrogen, which gases serve in a certain measure to dilute the ammonia. As a certain dilution of that product is necessary for the success of the operation, I will here at once state that it may be effected at will by adding to substances abounding in nitrogen, a greater or less proportion of a non-nitrogenous body—of pure sugar, for instance.

The ammonia is determined by receiving it in hydrochloric acid, converting the chloride of ammonium formed into bichloride of platinum and chloride of ammonium, which is then either weighed at once, or ignited, and its quantity, respectively that of the ammonia and of the nitrogen, calculated from the residuary metallic platinum. Many nitrogenous organic compounds give upon ignition with soda-lime no ammonia, but yield other nitrogenous volatile bases free from oxygen; thus indigo blue yields aniline; narcotine, morphia, quinine, and cinchona yield new volatile bases. All these volatile bases have, like ammonia, the property of forming double salts with hydrochloric acid and bichloride of platinum. Now, it would be committing a serious blunder to take these double salts for ammonio-bichloride of platinum, weigh them as such, and calculate the nitrogen from the weight found. By igniting them, and calculating the nitrogen from the residuary metallic platinum, all error is avoided, as these bases, like ammonia, contain in the double salts which they form with bichloride of platinum, to each equivalent of platinum 1 equivalent of nitrogen (*Liebig*). The other parts of the practical process (the collection and determination of the ammonia) require no theoretical explanation.

aa. Apparatus and other objects required for the Process.

1. The objects enumerated § 174, for weighing and mixing the substance.

2. A Combustion Tube of the kind described § 174, 3 (with beak turned upward, and rounded edges at the orifice); length about 40 centimetres, width about 12 millimetres. The combustion is effected in an ordinary combustion furnace (§ 174, 12).

3. Soda-Lime.—A mixture of caustic lime with hydrate of soda (§ 66, 5). It is advisable to gently heat in a platinum or porcelain dish, a quantity of the soda-lime sufficient to fill the combustion tube, so as to have it perfectly dry for the process of combustion. In the analysis of non-volatile substances, the best way is to use the soda-lime while still warm.

4. Asbestos.—A small portion of this substance is ignited in a platinum crucible previous to use.

5. A Varrentrapp and Will's Bulb Apparatus, as illustrated in Fig. 123.

This may be procured at any chemical apparatus and instrument warehouse. It is filled with hydrochloric acid of 1·13 specific gravity to the level indicated in the drawing, either by dipping the point into the acid, and applying suction to *d*, or by means of a pipette.

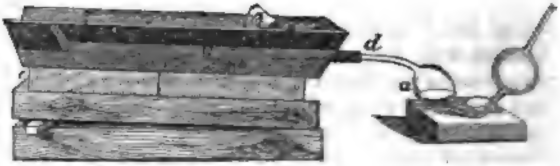

Fig. 123.

6. A soft, well-perforated CORK, which fits the combustion tube air-tight, and in which the tube *d* of the bulb apparatus fits closely.

7. A SUCTION TUBE filled with hydrate of potassa, and closed at the anterior end with a perforated cork, through which the point of the bulb apparatus passes.

The reagents, &c., required for the ulterior treatment of the fluid obtained in the process of combustion, are omitted here, as it is not necessary to have them ready at the beginning of the operation.

bb. THE PROCESS.

The combustion tube is half-filled with soda-lime, which is then gradually transferred to the perfectly dry, and, if the nature of the substance permits, still warm mortar, where it is most intimately mixed with the weighed substance (compare § 175), forcible pressure being carefully avoided; a layer of soda-lime, occupying about 3 centimetres, is now introduced into the posterior part of the combustion tube, and the mixture filled-in after; the latter, which will occupy about 20 centimetres of the length of the tube, is followed by a layer of about 5 centimetres of soda-lime, which has been used to rinse the mortar, and this again by a layer of about 10 or 12 centimetres of pure soda-lime, leaving thus about 4 centimetres of the tube clear. The tube is then closed with a plug of loose asbestos, and a free passage for the evolved gases formed by a few gentle taps; it is then connected with the bulb apparatus by means of the perforated cork, and finally placed in the combustion furnace (see Fig. 123).

To ascertain whether the apparatus closes air-tight, some air is expelled by holding a piece of red-hot charcoal to the bulb *a*, and the apparatus observed, to see whether the liquid will, upon cooling, permanently assume a higher position in *a* than in the other limb. The tube is then gradually surrounded with ignited charcoal, commencing at the anterior part, and progressing slowly towards the beak the operation being conducted exactly as in an ordinary combustion (§ 175). Care must be taken to keep the anterior part of the tube tolerably hot throughout the process, since this will almost entirely prevent the formation of liquid carbides of hydrogen, the presence of which in the hydrochloric acid would be inconvenient. The asbestos should be kept sufficiently hot to guard against its retaining water, and with this, ammonia. The combustion should be conducted so as to maintain a steady and uninterrupted evolution of gas; there is no fear of any ammonia escaping unabsorbed, even if the evolution is rather brisk; whilst the analysis runs some risk from the receding of the hydrochloric acid, which inevitably takes place the very moment the evolution of gas ceases, and this, in some instances, with such impetuosity as to force the acid into the combustion tube, which of course spoils the whole analysis. When operating upon compounds abounding in nitrogen, even the greatest care in conducting the process will prove unavailing against the powerful affinity of the hydrochloric acid for the ammoniacal gas in the tube. This may be readily prevented, however, by mixing with the substance an equal quantity of sugar, which will give rise to the evolution of more permanent gases diluting the ammonia.

When the tube is ignited in its whole length, and the evolution of gas has *totally* ceased,* the point of the combustion tube is broken off, and a certain volume of air (three or four times the capacity of the tube) is sucked through the apparatus, to force the last traces of ammonia into the hydrochloric acid; to guard against the inhalation of acid fumes, the suction tube is filled with hydrate of potassa, or a small aspirator is used.

Liquid nitrogenous compounds are weighed in small sealed glass bulbs, and the process is conducted as directed § 181 (determination of carbon), with this difference, that soda-lime is substituted for oxide of copper. It is advisable to employ tubes of greater length for the combustion of liquids than are required for solid nitrogenous bodies. The best method of conducting the operation, is to heat first about one-third of the tube at the anterior end, and then to force the liquid from the bulbs into the tube by heating the hinder end of the latter; the expelled liquid will thus become diffused in the central part of the tube, without being decomposed. By a progressive application of heat, proceeding slowly from the anterior to the posterior end, a steady and uniform evolution of gas may be easily maintained.

When the combustion is terminated, the bulb apparatus is emptied, through the opening at the point, into a small porcelain dish, and rinsed with water until the rinsings cease to manifest acid reaction. If liquid carbides of hydrogen have been formed, the fluid is passed through a moistened filter to separate them. Solution of *pure* bichloride of platinum† in excess, is added to the filtrate, and the mixture evaporated to dryness on a water-bath; the residue is treated with a mixture of 2 volumes of strong alcohol and 1 volume of ether. If the fluid acquires a bright yellow color, this may be taken as a proof that the quantity of bichloride of platinum added was sufficient for the intended purpose; if not, a fresh portion of the substance (best in alcoholic solution) must be added.‡ The residuary double salt of bichloride of platinum and chloride of ammonium is finally collected upon a weighed filter, which has been dried at 212° F., washed with the above-mentioned mixture of alcohol and ether, dried, and weighed (compare § 99, 2). The dried filter is weighed best between two close-fitting watch-glasses held together by a clasp. The bichloride of platinum and chloride of ammonium so obtained is not invariably of a pure bright yellow color, but sometimes of a darker or brownish yellow. This is the case more especially with difficultly combustible substances abounding in carbon, as it is less easy in such cases to avoid the formation of fluid carbides of hydrogen, which blacken the hydrochloric acid in the process of evaporation. Direct experiments have proved, however, that this coloration does not perceptibly impair the accuracy of the results. The purity of the bichloride of platinum and chloride of ammonium may be ascertained by reducing it to metallic platinum, according to the directions given in § 99, 2.

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* This is indicated by the white color which the mixture re-assumes when the carbon deposited on the surface is completely oxidized.

† If the bichloride of platinum contains an admixture of chloride of potassium or chloride of ammonium, an excess of nitrogen is the result; if it contains an admixture of nitric acid, this will, during the evaporation, cause the formation of chlorine and the consequent destruction of a portion of the ammonia, and accordingly too little nitrogen will be obtained. It is therefore always necessary to ascertain the purity of the bichloride of platinum.

‡ As the double salts of platinum with some of the volatile bases produced in the decomposition of many nitrogenous organic substances (see above), are more readily soluble in alcohol than ammonio-bichloride of platinum, ether mixed only with a few drops of alcohol is used as washing fluid, instead of the mixture of alcohol and ether, if there is reason to suspect that such double salts of platinum are present (*A. W. Hofmann*).

The results are very accurate; usually somewhat too low rather than too high (about 0·1—to 0·2 per cent.), which is owing to traces of chloride of ammonium escaping condensation in the absorption apparatus, and being carried off with the permanent gases, as is observed in every analysis of the kind. If, as is sometimes the case, the results are too high, this is principally owing to the impurity of the bichloride of platinum.

γ. *Péligot's Modification of Varrentrapp and Will's Method.*

§ 187.

The essential part of this modification consists in this, that the ammonia generated in the process of combustion with soda-lime, instead of being conducted into hydrochloric acid, is received in a measured quantity of sulphuric acid or oxalic acid of known strength; the amount of free acid remaining being then determined by neutralizing with a solution of soda of known strength, and calculating from the difference the amount of acid saturated by the ammonia, and accordingly also the quantity of the latter (compare § 99, 3).

The most convenient way is to use the standard oxalic or standard sulphuric acid, of § 215. 10 c.c. of this, containing 0·63 of crystallized oxalic acid or 0·40 of hydrated sulphuric acid, and corresponding accordingly to 0·17 of ammonia, or 0·14 of nitrogen, will generally suffice for the analysis of 0·5 grm. of a substance containing 10—20 per cent. of nitrogen.

The apparatus is the same as in β (Fig. 123). The acid is accordingly measured into a beaker; the point of the bulb apparatus is then immersed in the acid, and as much as possible of the latter sucked into the bulb; the acid adhering to the point is rinsed off. When the combustion is completed, the bulb apparatus is emptied into the same beaker and properly rinsed; the fluid is then neutralized. The solution of soda must be perfectly free from carbonic acid. I prefer diluting it, so that about 3 c.c. of it saturate 1 c.c. of the acid.

This method is particularly well suited for technical and agriculturo-chemical investigations. With accurate measuring vessels, properly prepared standard fluids, and skilful manipulation, it gives results hardly less accurate than the method described in § 186.

C. ANALYSIS OF ORGANIC COMPOUNDS CONTAINING SULPHUR.

§ 188.

The usual method of determining the carbon in organic bodies—viz., by combustion with oxide of copper or chromate of lead—would give results too high in the analysis of compounds containing sulphur; since—more especially if oxide of copper is used as oxidizing agent—a portion of the sulphur would be converted in the process into sulphurous acid, which would be absorbed with the carbonic acid in the potassa-apparatus. To remedy this defect, a tube 10—20 centimetres long, filled with perfectly dry binoxide of lead, is placed between the chloride of calcium tube and the potassa-apparatus. The binoxide of lead completely absorbs the sulphurous acid, forming sulphate of lead ($PbO_2 + SO_2 = PbO, SO_3$); and thus the carbonic acid alone finds its way to the potassa-apparatus. No sulphurous acid remains in the chloride of calcium tube, if the latter is left undisturbed until the water has combined with the chloride of calcium to crystallized chloride of calcium. It is advisable after this to draw some dried air through the tube. The presence of sulphur demands no modification in the processes described §§ 185, 186, and 187, for the determination of nitrogen. As regards the quantitative estimation of the sulphur in organic compounds, that element is invariably weighed in the form of sulphate of baryta, into which it may be converted either in the dry or in the moist way. In substances containing oxygen in presence of sulphur, the oxygen is estimated from the loss.

a. Methods in the Dry Way.

1. *Method suitable, more particularly, to determine the Sulphur in non-volatile substances poor in Sulphur, e.g., in the so-called Protein Compounds (Liebig).*

Put some lumps of hydrate of potassa, free from sulphuric acid, (§ 66, 8, *c*), into a capacious silver dish, add $\frac{1}{8}$ of pure nitrate of potassa, and fuse the mixture, with addition of a few drops of water. When the mass is cold, add to it a weighed quantity of the finely pulverized substance, fuse over the lamp, stir with a silver spatula, and increase the heat, continuing the operation until the white color of the mass shows that the carbon separated at first has been completely consumed. Should this occupy too much time, you may accelerate it by the addition of nitrate of potassa in small portions. Let the mass cool, then dissolve in water, supersaturate the solution with hydrochloric acid in a capacious beaker covered with a glass dish, and precipitate with chloride of barium. Wash the precipitate well with boiling water, first by decantation, then on the filter. Dry and ignite. Treat the ignited sulphate of baryta as directed § 132, I., 1, for very accurate analyses; if this latter operation is omitted, the result is almost always too high.

2. *Method adapted more particularly for the Analysis of non-volatile or difficultly volatile substances containing more than 5 per cent. of Sulphur (Kolbe,* "Supplemente zum Handwörterbuch," p. 205).

Introduce into the posterior part of a straight combustion tube,* 40—45 centimetres long, a layer, 7—8 centimetres long, of an intimate mixture of 8 parts of pure anhydrous carbonate of soda, and 1 part of pure chlorate of potassa; after this introduce the weighed substance to be analysed, then another layer, 7 or 8 centimetres long, of the same mixture; mix the organic compound intimately with the carbonate of soda and chlorate of potassa, by means of the mixing wire (Fig. 104

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* Sealed and rounded at the end like a test tube.

§ 176), to ensure its equal distribution through the entire mass; fill up the still vacant part of the tube with anhydrous carbonate of soda or potassa mixed with a little chlorate of potassa. Clear a *wide* passage from end to end by a few gentle taps, place the tube in a combustion furnace, heat the anterior part to redness, and then, progressing slowly towards the posterior part, proceed to surround with red-hot charcoal the part occupied by the mixture with the organic compound. In the analysis of substances abounding in carbon, it is advisable to introduce into the posterior part of the tube a few lumps of pure chlorate of potassa, to ensure complete combustion of the carbon, and perfect conversion into sulphates of the compounds of potassa with the lower oxides of sulphur that may have formed. The sulphuric acid in the contents of the tube is determined as in 1.

3. *Method adapted for the Analysis both of non-volatile and volatile Substances, but more especially the latter* (*Debus*, "Annal. d. Chem. und Pharm.," 76, 90.)

Dissolve 1 equivalent (149 parts) of bichromate of potassa purified by recrystallization, and 2 equivalents of carbonate of soda (106 parts), in water, evaporate the solution to dryness, reduce the lemon-colored saline mass ($KO, CrO_3 + Na\,O, Cr\,O_3 + NaO, CO_2$) to powder, heat to intense redness in a hessian crucible, and transfer still hot to a filling tube* (Fig. 101, § 176). When the powder is cold, introduce a layer of it, 7—10 centimetres long, into a common combustion tube; then introduce the substance, and after this another layer, 7—10 centimetres long, of the powder. Mix intimately by means of the mixing wire, then fill the still unoccupied part of the tube with the carbonate of soda and chromate of potassa mixture, and apply heat as in an ordinary ultimate analysis. When the entire mass is heated to redness, conduct a slow stream of dry oxygen gas over it for ½—1 hour. When cold, brush the ash off the tube, cut the latter into several pieces over a sheet of paper, transfer the pieces to a beaker, and pour over them a sufficient quantity of water to dissolve the saline mass. Add hydrochloric acid in tolerable excess, then some alcohol, and apply a gentle heat until the solution shows a beautiful green color; filter the fluid from the sesquioxide of chromium produced by the combustion (this contains sulphuric acid); wash first with water containing hydrochloric acid, then with alcohol, dry, and transfer the dry sesquioxide of chromium to a platinum crucible; add the filter ash, mix with 1 part of chlorate and 2 parts of carbonate of potassa (or soda), and ignite until the sesquioxide of chromium is completely converted into chromate of potassa (or soda). Dissolve the fused mass in dilute hydrochloric acid, and reduce by heating with alcohol; add the solution to the fluid filtered from the sesquioxide of chromium, heat the mixture to boiling, and precipitate the sulphuric acid with chloride of barium. *Debus* obtained by this method very satisfactory results (99·76 and 99·50 instead of 100 of sulphur) in the experimental analysis of substances of known composition; thus he obtained 30·2 of sulphur in the *Xanthogenamide*, instead of 30·4, &c.

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* The saline mass must always first be examined to ascertain whether it is quite free from sulphur. For this purpose, a small portion of it is reduced with hydrochloric acid and alcohol, chloride of barium added, and the mixture allowed to stand 12 hours at rest; it is then carefully examined to ascertain whether or not traces of a precipitate are visible.

4. *Method equally adapted for the Analysis of Solid and Liquid Volatile Compounds. J. Russell* ("Journ. f. prakt. Chem.," 64, 230); suggested by *Bunsen.*

Introduce into a combustion tube, 40 centimetres long, sealed at the posterior end, first 2—3 grammes of pure oxide of mercury, then a mixture of equal parts of oxide of mercury and pure anhydrous carbonate of soda, mixed with the substance, and fill up the tube with the carbonate of soda mixed with a little oxide of mercury. Connect the open end of the tube with a gas delivery tube dipping under water, to effect the condensation of the mercurial fumes. Protect the part of the tube occupied by the substance by a screen, then heat the anterior part to bright redness, and keep it so during the entire process. At the same time, heat another portion of the tube, nearer to the end, but not to the same degree of intensity, so that there may be alternate parts in the tube in which the oxide of mercury is left undecomposed. When the part before the screen is at bright redness, remove the screen, heat the mixture containing the substance, regulating the application of heat so as to ensure complete decomposition in the course of 10—15 minutes, and heat at the same time the still unheated parts of the tube, and lastly also the pure oxide of mercury at the extreme end. The gas must be tested from time to time, to ascertain whether it contains free oxygen. Dissolve the contents of the tube in water, add some chloride of mercury, to decompose the sulphide of sodium which may have formed, acidify with hydrochloric acid, oxidize the sulphide of mercury which may have formed, with chlorate of potassa, and finally precipitate the sulphuric acid with chloride of barium. *J. Russell* obtained by this method very satisfactory results in the analysis of pure sulphur, sulphocyanide of potassium, and bisulphide of carbon.

b. Method in the Moist Way.

According to *Beudant, Daguin* and *Rivot* ("Compt. rend.," 1853, 835, "Journ. f. prakt. Chem.," 61, 135), the sulphur in organic compounds may be readily determined by heating with pure solution of potassa, adding 2 volumes of water and conducting chlorine into the fluid. When the oxidation is effected, the acidified solution is freed from the excess of chlorine by application of heat, then filtered, and the filtrate precipitated with chloride of barium. Mr. *C. J. Merz*, of my laboratory, has employed both this method and *Liebig's* (*a*, 1) in the analysis of fine horn shavings, with very satisfactory results. He obtained, in two experiments by *Liebig's* method, 3·37 and 3·345 in 100 parts of horn dried at 212° F.; in two other experiments by *Beudant, Daguin* and *Rivot's* method, 3·31 and 3·33 per cent.

⁂ Substances leaving ash on incineration, and which may therefore be presumed to contain sulphates, are boiled with hydrochloric acid; the solution obtained is filtered, and the filtrate tested with chloride of barium.

If a precipitate of sulphate of baryta forms, the sulphur contained in it is deducted from the quantity found by one of the methods described above; the difference gives the quantity of the sulphur which the analysed substance contains in organic combination.

D. DETERMINATION OF PHOSPHORUS IN ORGANIC COMPOUNDS.

§ 189.

Mulder, who has occupied himself more than any other chemist with the determination of phosphorus in organic substances, recommends the following method:—

Dissolve a weighed portion of the substance by boiling with hydrochloric acid; filter, if necessary, and determine the phosphoric acid which the fluid may contain, by *Berthier's* method (§ 134, I., *d*). Boil another weighed portion of the substance with nitric acid, and treat the fluid in the same way as the hydrochloric acid solution. If you find in both the same per-centage amount of phosphoric acid, the analysed substance contains the phosphorus only in the form of phosphoric acid; but if you obtain a larger proportion of acid in the second experiment than in the first, the difference indicates the quantity of phosphoric acid formed by the action of the nitric acid upon phosphorus contained in the analysed compound in the non-oxidized state. Thus, for instance, *Mulder* found in caseine in both experiments 3·5 per cent. of phosphoric acid, whilst in the analysis of albumen the hydrochloric acid solution gave 0·35 per cent., the nitric acid solution 0·78 per cent. of that acid.

The phosphorus cannot be determined by incineration of the substance and examination of the ash. Vitellin, which, when treated with nitric acid, gives 3 per cent. of phosphoric acid, yields barely 0·3 per cent. of ash (*Baumhauer*).

The methods described in § 188, *a*, 1, 2, 4, and *b*, may also be employed to determine the total quantity of phosphorus in organic compounds.

E. ANALYSIS OF ORGANIC COMPOUNDS CONTAINING CHLORINE (BROMINE OR IODINE).

§ 190.

The combustion of organic compounds containing chlorine with oxide of copper gives rise to the formation of subchloride of copper, which, were the process conducted in the usual manner, would condense in the chloride of calcium tube, and would thus vitiate the determination of the hydrogen. This and every other defect may be readily remedied, however, by substituting chromate of lead for oxide of copper, and conducting the process exactly as directed § 177. The chlorine is, in that case, converted into chloride of lead, and retained in that form in the combustion tube.

If the combustion is effected with oxide of copper in a current of oxygen gas, the subchloride of copper formed is decomposed by the oxygen into oxide of copper and free chlorine, which latter element is retained partly in the chloride of calcium tube, partly in the potassa-apparatus. To remedy this defect, *Städeler* ("Annal. d. Chem. u. Pharm.," 69, 335) proposes to retain the chlorine in the tube, by filling the anterior part of the latter with clean copper turnings, to be kept red hot during the process of combustion, and arresting the current of oxygen the moment the copper turnings begin to oxidize. According to *A. Völcker* ("Chem. Gaz.," 1849, 245), the evolution of chlorine may be avoided, by adding to the oxide of copper $\frac{1}{8}$ of oxide of lead.

As regards the determination of the chlorine in organic compounds containing that element, this is invariably effected by igniting the substance with alkalies or alkaline earths, by which process all the chlorine is obtained as chloride.

Lime free from chlorine (which is easily obtained by the calcination of marble) is usually employed as a decomposing agent; the lime used must always be carefully tested, to make quite sure that it contains no chlorine.

Introduce into a combustion tube, about 40 centimetres long, the posterior end of which is sealed and rounded like a test tube, a layer of lime, 6 centimetres long, then the substance, after this another layer of lime, 6 centimetres long, and mix intimately with the wire; fill the tube almost to the mouth with lime, clear a free passage for the evolved gases by a few gentle taps, and apply heat in the usual way. If you have to operate upon volatile fluids, introduce them into the tube in small glass bulbs. When the decomposition is terminated, dissolve in dilute nitric acid, and precipitate with solution of nitrate of silver (§ 141). *Kolbe* recommends the following process to obtain the contents of the combustion tube: when the decomposition is completed, remove the charcoal, insert a cork into the open end of the tube, brush away every particle of ash, and immerse the tube still hot, with the sealed end downwards, into a beaker filled two-thirds with distilled water; the tube breaks into many pieces, and the contents are then more readily acted upon. As in this method the ignition of compounds abounding in nitrogen may be attended with formation of cyanide of calcium or cyanide of sodium, the separation of the chloride and cyanide of silver, if required, is to be effected by the process given in § 169, 6, *b* (*Neubauer* and *Kerner*, "Annal. d. Chem. u. Pharm.," 101, 324, 344).

In the analysis of acid organic compounds containing chlorine (*e.g.*, chlorospiroylic acid), the chlorine may often be determined in a simpler manner, viz., by dissolving the substance under examination in an excess of dilute solution of potassa, evaporating to dryness, and igniting the residue, by which means the whole of the chlorine present is converted into a soluble chloride (*Löwig*).

Organic compounds containing bromine or iodine are analysed in the same manner as those containing chlorine.

F. ANALYSIS OF ORGANIC COMPOUNDS CONTAINING INORGANIC BODIES.

§ 191.

In the analysis of organic compounds containing inorganic bodies, it is, of course, necessary first to ascertain the weight of the latter before proceeding to the determination of the carbon, &c., as otherwise the amount of the organic substance, whose constituents have furnished the carbonic acid, water, &c., not being known, it would be impossible to estimate the quantity of oxygen from the loss.

If the organic bodies in question are salts or similar compounds, their bases are determined by the methods given in the Fourth Section; but in cases where the inorganic admixtures are of a nature to be regarded more or less as impurities (*e.g.*, the ash in wheaten flour), they may usually be determined with sufficient accuracy by the combustion of a weighed portion of the substance in an obliquely placed platinum crucible, or in a platinum dish, with use of a cylinder to promote the draught (see "Analysis of Ashes). In the analysis of substances containing fusible salts, even long continued ignition will often fail to effect complete combustion, as the carbon is protected by the fused salt from the action of the oxygen. In such cases, the best way to effect the purpose is to carbonize the substance, treat the mass with water, and incinerate the undissolved residue; the aqueous solution is, of course, likewise evaporated to dryness, and the weight of the residue added to that of the ash (compare Special Part, "Analysis of Ashes").

If organic compounds whose ash contains potassa, soda, baryta, lime, or strontia, are burnt with oxide of copper, part of the carbonic acid evolved remains combined with the alkalies or earths. As, in many cases, the amount of carbonic acid thus retained is not constant, and the results are, moreover, more accurate if the whole amount of the carbon is expelled and determined as carbonic acid, the oxide of copper is mixed with substances which will effect the decomposition of the carbonates at a high temperature, *e.g.* teroxide of antimony, phosphate of copper, boracic acid (*Fremy*), &c.; or the combustion is effected with chromate of lead, with addition of $\frac{1}{10}$th of bichromate of potassa, according to the directions given in § 177. The latter method deserves the preference. Accurate experiments have shown that in a combustion effected with chromate of lead and bichromate of potassa, not a trace of carbonic acid remains with the bases.

If the organic substance containing such fixed constituents, is weighed in a small porcelain or platinum boat, the ash, carbon, and hydrogen may be determined in one and the same portion. The amount of carbonic acid contained in the ash is added to that found by the process of combustion; if the carbonic acid in the ash cannot be calculated, as in the case of carbonates of the alkalies, it may be determined by means of fused borax (§ 139, II., *d*).

III. DETERMINATION OF THE EQUIVALENT OF ORGANIC COMPOUNDS.

The methods of determining the equivalent of organic compounds differ essentially according to the nature and properties of the various compounds. There are three general methods in use for this purpose, viz.:—

§ 192.

1. *We take a Substance of known Equivalent and determine the exact quantity of it which forms a Definite and well characterized Compound with the Body whose Equivalent we wish to Determine.*

This method is pursued in determining the equivalent of the organic acids and organic bases, and of many indifferent bodies possessed of the property of combining with bases. We occupy ourselves here simply with the analytical process; the mode of calculating the equivalent from the results obtained will be found in the chapter on the Calculation of Analyses.

a. The equivalent of *organic acids* is, in most cases, determined from the silver salt of the acid, because the analysis of this is very simple, and there is almost always the positive certainty that the analysed salt is not a basic or hydrated compound. Other salts also are, however, frequently used for the same purpose, particularly the lead, baryta, and lime salts of organic acids. In the analysis of the lead salts of organic acids, especial care must be taken not to mistake basic for neutral, nor in the analysis of the baryta and lime salts, hydrated for anhydrous salts. For the manner in which the quantitative determination of the bases in question is effected, I refer to Section IV.

b. The equivalent of *organic bases* forming crystallizable salts with sulphuric acid, hydrochloric acid, or any other easily determined acid, is best ascertained by estimating, by the usual methods, the proportion of the acid contained in a weighed amount of the salt.

If the salts do not crystallize, a known quantity of the dried alkaloid is introduced into a drying tube (Fig. 124), which is then accurately weighed with its contents; a slow current of dry hydrochloric acid gas is transmitted through the apparatus for some time; the tube ultimately heated to 212° F. (see § 28, Fig. 29), and a stream of atmospheric air transmitted through it; the quantity of the hydrochloric acid absorbed is found from the increase in the weight of the tube. The accuracy of the results may be controlled by dissolving the hydrochlorate in water, and precipitating the chlorine from the solution by nitrate of silver. The equivalent of the alkaloids may be determined also from the insoluble double salts produced by precipitating the solution of their hydrochlorates with bichloride of platinum; the double chlorides thus produced are cautiously ignited, § 124, and the residuary platinum accurately weighed.

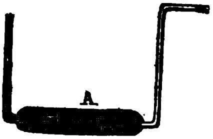

Fig. 124.

c. In the case of *indifferent bodies*, there is usually no other choice left than to determine the equivalent from the lead-compound; since these substances either altogether refuse to enter into combination with other bases besides lead, or form with them compounds only which cannot be obtained in a state of purity. Although the determination of the equivalent of an indifferent body from the compound which the latter forms with lead, is liable to leave the matter in doubt, as the oxide of lead will often combine with such substances in varying proportions, yet the analysis of such compounds is always interesting in this—that we learn by it whether the organic body combines with the lead without alteration, or gives up water upon entering into combination with that metal. Organic substances will also occasionally form with water solid and crystallizable compounds, by the analysis of which the equivalent of the organic body may be determined.

§ 193.

2. The Specific Gravity of the Vapor of the Compound is determined (Dumas).

The following are the outlines of *Dumas'* method, which I shall immediately after proceed to describe more in detail. A light glass globe, filled with dry air, and the exact capacity of which is afterwards ascertained, is accurately weighed; the weight of the air in the globe is calculated at the temperature and atmospheric pressure observed during the process of weighing, and the result subtracted from the first weight: the difference expresses the weight of the exhausted vessel. A more than sufficient quantity of the substance, the density of the vapor of which it is intended to determine, is then introduced into the globe, and exposed to a uniform temperature exceeding the boiling point of the substance, until the latter is completely converted into vapor, and the excess expelled together with the atmospheric air originally contained in the globe; the vessel is then sealed air-tight, and accurately weighed. The difference between the weight found and that of the exhausted globe, expresses the exact weight of a volume of the vapor corresponding to the capacity of the globe; supplying thus the necessary data for calculating the density of the vapor.

It is hardly necessary to remark that the volume of the vapor must first be calculated at the usual height of the barometer, and 32° F. of the thermometer, and consequently that the state of the barometer and thermometer must be correctly noted both during the first weighing and at the time of sealing the glass globe.

This method is of course applicable only to substances which volatilize without suffering decomposition. To obtain accurate results, it is indispensable that the examined substance be perfectly pure.

I will now proceed to describe the analytical process; for the manner of correcting and calculating the results, and inferring the composition of the analysed bodies from them, I refer to the chapter on the "Calculation of Analyses" (§ 204).

a. Apparatus and other Requisites.

1. THE SUBSTANCE.—From 6 to 8 grammes are required. The boiling point of the substance must be pretty accurately known.

2. A LIGHT GLASS GLOBE WITH DRAWN-OUT NECK.

A light globe of pure glass is selected, free from flaws and holding from 250 to 500 cubic centimetres; it is carefully rinsed with water, and then thoroughly dried. After this, it is completely exhausted, dry air readmitted into it, and the same operation repeated several times (the apparatus illustrated in Fig. 97, § 175, is used for this purpose). The neck of the globe is then softened near the bulb, and drawn out in the shape represented in Fig. 125.

The extreme point is cut off, and the edges slightly rounded over the the spirit-lamp; this point having to be sealed air-tight with the greatest despatch, at a subsequent stage of the process, it is advisable to ascertain, in the first place, whether the glass of the globe is readily fusible or not; this may be done by trying to seal the point of the original neck of the balloon, previous to drawing it out; should this present any difficulty, the globe is totally unfit for the intended purpose.

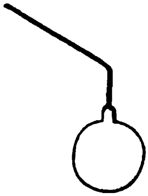

Fig. 125.

3. A SMALL IRON OR COPPER VESSEL for the reception of the fluid in which the globe is to be heated (see Fig. 126). The fluid which is to serve as *bath* must admit of being heated to at least 54° or 72° F. beyond the boiling point of the substance under examination. Oil will answer the purpose in all cases where a temperature higher than that of boiling water is required; however, a chloride of calcium bath—if its temperature, which in a perfectly saturated bath may be raised to 356° F., is sufficiently high for the purpose—is more convenient than an oil-bath, as the globe may be more easily cleaned.

4. AN APPARATUS TO KEEP THE GLOBE IN POSITION.—This may be

readily made with a handle and some iron wire. During the operation, it is attached to a retort stand (see Fig. 126).

5. A quantity of MERCURY more than sufficient to fill the globe.

6. An accurately GRADUATED TUBE of about 100 cubic centimetres capacity.

7. SPIRIT-LAMP and BLOWPIPE.

8. A correct BAROMETER.

9. A correct THERMOMETER, capable of indicating the highest degree of heat the case under examination may require.

b. The Process.

α. Weigh the globe on the balance, placing a thermometer inside the case. Leave the globe for 10 minutes on the scale, to ascertain whether its weight remains constant. If so, the weight is noted, together with the height of the barometer, and the temperature indicated by the thermometer inside the case.

β. Introduce about 8 grammes of the fluid or, by the application of a gentle heat, liquefied substance into a glass; heat the globe gently, and dip the pointed end deep into the liquid. If the substance under examination has a high fusing point, the neck and point of the globe likewise require heating, to guard against the fluid solidifying in the neck. As soon as the globe cools—which, in the case of very volatile substances, is accelerated by dropping ether upon it—the fluid enters and spreads in it. Do not introduce more than 5—7 grammes.

γ. Heat the contents of the vessel (3) to 104°—122° F., and immerse the globe by means of the apparatus (4), and also a thermometer, in the bath as shown in Fig. 126.

Raise the temperature of the bath to the required point.* As soon as the temperature in the globe is somewhat higher than the boiling point of the substance, the vapor of the latter rushes out through the orifice of the neck; the force of the current increases at first with the temperature of the bath, but diminishes afterwards by degrees, and ceases finally altogether (after about 15 minutes). Should any of the vapor have condensed into drops in the point of the neck projecting above the surface, these may be at once reconverted into vapor, by moving a piece of red-hot charcoal to and fro round it. The moment that a perfect equilibrium is fully established at the desired temperature, seal the point of the globe hermetically, by means of a spirit-lamp and blowpipe, and note immediately after the height of the thermometer. To ascertain whether or not the point is hermetically sealed, you need simply direct a current of air through the blowpipe upon the

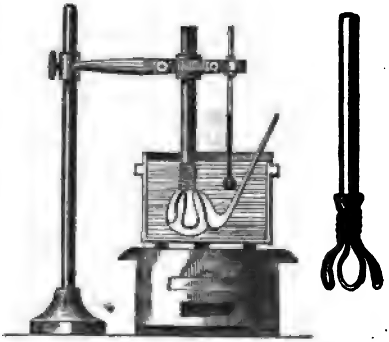

Fig. 126.

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[*] If the globe is immersed in a chloride of calcium or oil-bath, you must endeavor to maintain a uniform temperature towards the end of the process, which may be easily effected by properly regulating the heat.

projecting point of the neck: if the tube is closed hermetically, a small portion of the vapor condenses, forming a column of fluid, which is retained in the end of the tube by capillary attraction; this is not observed if the tube is not hermetically sealed. The height of the barometer also is noted again, if it has changed since the first observation.

δ. Remove the sealed globe from the bath, allow to cool, wash most carefully, wipe perfectly dry, and weigh again in the same manner as before.

ε. Immerse the pointed end of the globe in its entire length in mercury, scratch a mark with a file near the end, and break off the point; whereupon the mercury will immediately rush into the globe, a vacuum having been created in it by the condensation of the vapor. In this operation, place the glass globe in the hollow of your hand, and rest the latter upon the edge of the mercurial trough. If the globe, at the moment of sealing, was perfectly free from air, it will fill completely with mercury; otherwise an air bubble will remain in it. In either case transfer the mercury from the globe to the graduated tube (6), and measure accurately; if there was air in the globe at the moment of sealing it, fill it now with water, and measure also the volume of the latter liquid: the difference between the volume of the mercury and that of the water shows the volume of the air which had remained in the globe.

This method, if properly executed, gives nearly accurate results; for the manner of calculating the latter, I refer to the chapter on the "Calculation of Analyses" (§ 204).

§ 194.

3. A great many indifferent organic bodies absolutely refuse to combine with bases or acids, as, *e.g.*, salicine; or form with them only compounds, from which the equivalent of the organic body cannot well be determined, as *e.g.*, phloridzin. The equivalent of such substance is determined by producing by the action of acids, bases, halogens, &c., upon the body under examination, new compounds of known or ascertainable equivalents. Or, lastly, the equivalent is inferred from the manner in which the compound in question has been formed. In cases of this description, that equivalent is assumed to be the correct one which permits the most simple explanation of the processes of formation and decomposition.

This latter mode of determining the equivalent of substances is intimately connected with the higher branches of organic chemistry, and cannot be considered in detail here, as it is impossible to give universally applicable methods.

Supplement.

"ON THE USE OF GAS AS FUEL IN ORGANIC ANALYSIS."*

Dr. *Hofmann* has lately succeeded in providing our laboratories with a combustion furnace which has met with the general approval of chemists, and has been rapidly introduced into most of the English laboratories where gas furnishes the fuel for chemical operations. Its superiority over any of the proposed combustion furnaces is acknowledged by all who have recently adopted it.

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* By *A. W. Hofmann.* Extracted from the "Quarterly Journal of the Chemical Society," vol. vi. p. 209.

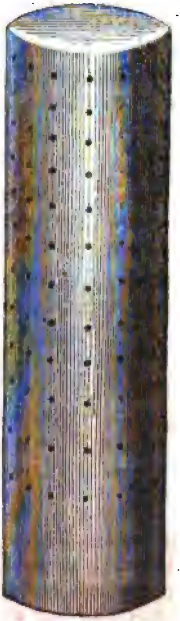

Fig. 127.

The construction of he apparatus being obvious from the accompanying wood-cuts, a few explanatory remarks will be sufficient. Into a brass tube, of from 3 feet to 3 feet 8 inches length, and 1 inch diameter (shown in section in Fig. 128), which communicates at both ends with the gas-main of the laboratory, there are screwed from twenty-four to thirty-four tubes. These tubes, $\frac{1}{3}$ inch thick and 7 inches high, are provided with stopcocks, and carry brackets, of $4\frac{1}{2}$ inches length and $\frac{5}{8}$-inch diameter, for the reception of five ordinary bat's-wing burners (each consuming from 3 to 4 cubic feet of gas per hour for a full luminous effect) upon which a corresponding number of clay-burners are fixed. The high clay burners, represented in Fig. 127, are 3 inches high, of $\frac{7}{8}$-inch exterior, and $\frac{3}{8}$-inch interior diameter. The perforations, which are of about the thickness of a pin, are made in rows; their number varies; those employed for Dr. Hofmann's furnace have ten rows, each of fifteen holes. From such a clay cylinder, loosely fixed upon an ordinary bat's-wing burner, the stopcock of which has been appropriately adjusted, the gas burns with a perfectly blue flame which envelopes the cylinder, and renders it in a short time incandescent.

The small burners are only $1\frac{3}{8}$ inches high, and have only seventy or eighty perforations. A row of these smaller burners serves as support for the combustion tube which is thus bedded in a channel of heated fire-clay. The system of brackets lying side by side acquires sufficient stability by a strong iron frame, which rests upon two firm supports, of cast iron, fastened down by screws upon the foot-plate, likewise of cast iron. The iron frame has moreover a groove for the reception of moveable side plates of fire-clay. They are of the same height as the high burners, over which they project, however, about $\frac{5}{8}$ inch, in consequence of their resting upon the frame; lastly, there are covering plates, likewise of fire-clay, which are supported by the side plates.

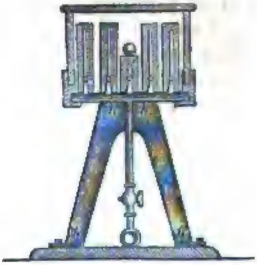

Fig. 128.

The whole disposition of this apparatus will be best understood by a glance at the perpective view given in Fig. 129.

In the front part, contiguous to the potassa-apparatus, the side plates and the covering plates are omitted, in order to show the disposition of the burners. During the combustion, however, all the burners are inclosed, as exhibited in the posterior part of the apparatus.

It deserves to be noticed that the efficiency of the furnace essentially depends upon the correct disposition of the gas-jets. The most appropriate space between the several burners, according to numerous experiments made for the purpose, is about $\frac{1}{8}$ inch. It is very important, for the attainment of a perfectly uniform temperature, that the several brackets bearing the burners should be equidistant. Their position is therefore specially secured by every bracket being fixed in an aperture formed in the iron frame, (Fig. 128).

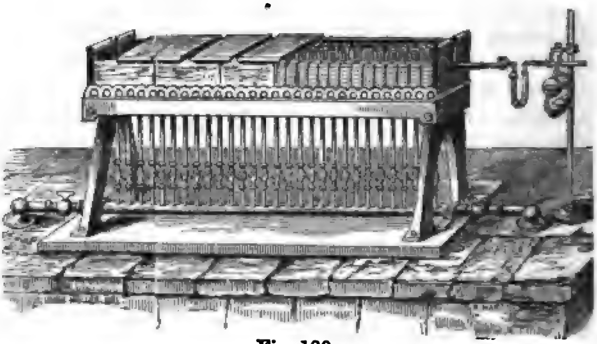

Fig. 129.

The use of the furnace scarcely requires any special remark. According to the length of the combustion tube, from 8 to 10 stopcocks (under all circumstances the largest possible number,) are opened at once at the commencement of a combustion. If care has been taken to regulate the amount of gas, either by the stopcocks in the horizontal gas-pipe, or by those in the separate supply-tubes, the lighted portion of the furnace, in 10 or 12 minutes, will be in a state of perfect incandescence, comparable only to the ignited mass of charcoal in an ordinary combustion furnace. After this it is only necessary to open the remainder of the stopcocks in appropriate succession, to insure a slow and regularly progressing combustion. The time required for the completion of an analysis varies from 40 minutes to an hour. Only in extraordinary cases a longer time may be required.

The heat obtained by this furnace is extremely uniform, and since it is conveyed to the combustion tube chiefly by radiation from the incandescent mass of surrounding clay, every part of the tube is equally heated. It is in this respect especially that the new apparatus differs from all former contrivances of this kind. The temperature which it is capable of yielding is entirely at the command of the operator. When strained to its full power, it gives a heat equal to that of the strongest charcoal combustion furnace, at which even the most refractory Bohemian tubes readily fuse; by appropriately adjusting the stopcocks, however, it is possible to maintain the furnace at any desired temperature, especially since it is only necessary to look into the channel, when, with a little practice, a correct idea of the temperature is rapidly obtained from the color of the glowing cylinders. It deserves, however, to be noticed, that the apparatus furnishes rather more than less heat than is generally required; it is preferable, therefore, under all circumstances, to protect the combustion tube by a metallic shield: for this purpose ordinary brass-wire gauze may be conveniently employed; which is more easily manipulated, and may be used longer than the thin copper or brass plate generally employed.

From what has been stated it is obvious that the furnace may be used in many operations in which charcoal has hitherto been considered almost indispensable. The combustion may be made with or without oxygen, as the case may necessitate. In all other tube operations, in passing gases or vapors through red-hot tubes (preparation of propylene gas), in reducing copper turnings, &c., the furnace may be used with equal advantage; for the latter operation, which occurs so frequently, it is found convenient to rearrange the burners in such a manner as to obtain, by the introduction of a second row of small burners in the place of large burners, two gutters or channels, in which two glass tubes, connected by means of caoutchouc with the same hydrogen-apparatus, may be heated at once. In like manner two combustion tubes, filled with a similar mixture, have been actually heated simultaneously. If short combustion tubes are to be heated, such as are used in nitrogen determinations, an additional advantage may be obtained by simultaneously operating on both sides of the apparatus.

One of the great advantages of this furnace is its durability. The clay burners are almost indestructible. The clay plates also, when well burnt, are very durable, and often serve for months, even after they are split. The mixture of gas and atmospheric air is so perfect, and the diffusion of the combustion is so great (the gas issuing from between 24,000 and 25,000 apertures), that neither upon the burners nor in the perforations is the slightest trace of carbon deposited.

It was found by experiment that a combustion, lasting one hour, and requiring the whole length of the furnace (34 rows of burners), consumes from 80 to 90 cubic feet; the maximum ever observed being 100 cubic feet. For a carbon determination, with 24 rows of burners, which generally lasts about 40 minutes, from 50 to 60 cubic feet are required; for nitrogen determination, from 25 to 30 cubic feet. Perfectly similar results have been observed by Dr. Forbes Watson. From these data it is obvious that this apparatus is a very economical one, especially in localities where gas is cheap and charcoal dear. In laboratories, therefore, where many combustions are made, the saving of fuel will readily cover the original outlay for the furnace.

The cost of the apparatus and the consumption of gas can be still further diminished by reducing the number of the rows of burners from 5 to 3. Fig. 130 shows the section of such a furnace, which has been used with good results.

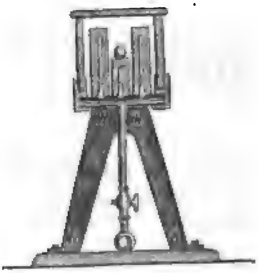

Fig. 130.

Such a furnace of course does not yield the same degree of temperature as the larger one, it also requires a few minutes more to produce the full effect; but in few cases will a higher temperature be necessary for combustions. Such a smaller apparatus is very useful in lectures, when a further simplification may be effected by a diminution of the number of the stopcocks.*

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* These furnaces are made by Mr. R. H. Hess, 16, John's Terrace, John Street, Kingsland Gate, N.

DIVISION II.

CALCULATION OF ANALYSES.

§ 195.

THE calculation of the results obtained by an analysis presupposes, as an indispensable preliminary, a knowledge of the general laws of the combining proportions of bodies, on the one hand, and of the more simple rules of arithmetic on the other. Chemical calculations do not necessarily require a complete knowledge of mathematics, as is often erroneously supposed: decimal fractions and simple equations will enable the student to make all the more common calculations. These remarks are not intended to dissuade students of chemistry and pharmacy from pursuing the study of the higher mathematics; I merely wish to encourage those who have had no opportunity of doing so, and who, as I have often experienced, are afraid to venture upon chemical calculations. For this reason, I have made the whole of the calculations given in the following paragraphs, in the most intelligible manner possible, and without logarithms.

I. *Calculation of the Constituent sought, from the Compound obtained in the Analytical Process, and exhibition of the Results in per cents.*

§ 196.

The bodies the weight of which it is intended to determine, are separated, as we have seen in the Part treating of the "Analytical Methods and Processes," either in the free state, or—and this most frequently—in combinations of known composition. The results are usually calculated upon 100 parts of the examined substance, since this gives a clearer and more intelligible view of the composition. In cases where the several constituents have been separated in the free state, the calculation may be made at once; but if the constituents have been separated in combination with other substances, they must first be calculated from the compounds obtained.

1. *Calculation of the per-centage Results, in Cases where the Substance sought has been separated in the Free State.*

a. Solid Bodies, Liquids, or Gases, which have been determined by Weight.

§ 197.

The calculation here is so exceedingly simple that I will give but one illustration.

Suppose you have analysed subchloride of mercury, and separated the mercury in the metallic state (§ 118, 1). 2·945 grammes of subchloride of mercury have given 2·499 grammes of metallic mercury.

$$2{\cdot}945 : 2{\cdot}499 :: 100 : x$$
$$x = 84{\cdot}85,$$

which means that your analysis shows 100 parts of subchloride of mercury to contain 84·85 of mercury, and consequently 15·15 of chlorine.

Now as the subchloride of mercury is known to consist of 2 equivalents of mercury and 1 equivalent of chlorine, and as the equivalent numbers of both these elements are also known, the true percentage composition of the body may be readily calculated from these data. When analysing substances of known composition for practice, the results theoretically calculated and those obtained by the analysis are usually placed in juxtaposition, as this enables the student at once to perceive the degree of correctness and accuracy with which the analysis has been performed.

Thus for instance—

	Found.	Calculated (compare § 84, *b*).
Mercury . . .	84·85	. . . . . 84·95
Chlorine . . .	15·15	. . . . . 15·05
	100·00	100·00

b. Gases which have been determined by Measure.

§ 198.

If a gas has been determined by measure, it is, of course, necessary first to ascertain the weight corresponding to the volume found, before the proportion of the gas in 100 parts by weight of the analysed substance can be calculated.

But as the exact weight of a certain definite volume of the various gases has been severally determined by minute and accurate experiments, this calculation also is a simple rule-of-three question, if the gas may be measured under the same circumstances under which the experiments were made by which the weight of a certain definite volume of it has been determined. The circumstances to be taken into consideration here, are:

Temperature and Atmospheric Pressure.

Besides these, the

Tension of the Aqueous Vapor

may also claim consideration in cases where water is used as the confining fluid, as the gas has been measured in the moist state.

The respective weights assigned in Table V.* to 1 litre of the gases there enumerated, refer to a temperature of 0° C. (= 32° F.), and an atmospheric pressure of 0·76 (760 millimetres) of mercury (= 29·9—30, inches of the English scale). We have, therefore, in the first place, to consider the manner in which volumes of gas measured at another temperature and another height of the barometer, are to be reduced to 0° of the centigrade thermometer, and 0·76 of the barometer.

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* See Tables at the end of the volume.

a. Reduction of a Volume of Gas of any given Temperature to 0° C., *or any other Temperature between* 0° *and* 100° C.

The following propositions regarding the expansion of gases were formerly universally adopted:

1. All gases expand alike for an equal increase of temperature.
2. The expansion of one and the same gas for each degree of the thermometer is independent of its original density.

Although the correctness of these propositions has not been fully confirmed by the minute investigations of *Magnus* and *Regnault*, yet they may be safely followed in reductions of the temperature of those gases which are most frequently measured in the course of analytical processes, as the co-efficients of the expansion of these gases scarcely differ from each other, and as there is never any very considerable difference in the atmospheric pressure under which the gases are severally measured.

The investigations just alluded to have given

. . . . 0·3665 . . .

as the co-efficient of the expansion of gases which comes nearest to the point; in other words, as the extent to which gases expand when heated from the freezing to the boiling point of water. They expand, therefore, for every degree of the centigrade thermometer

$$\frac{0{\cdot}3665}{100} = 0{\cdot}003665.$$

If we wish to ascertain how much space a cubic centimetre of gas at 0° C. will occupy at 10° C., we find

$$1 \times (1 + 10 \times 0{\cdot}003665) \textit{ i.e.} = 1{\cdot}03665.$$

If we wish to ascertain how much space 100 cubic centimetres at 0° C. will occupy at 10° C., we find

$$100 \times (1 + 10 \times 0{\cdot}003665) \textit{ i.e.}$$
$$100 \times 1{\cdot}03665 = 103{\cdot}665.$$

If we wish to know how much space 1 cubic centimetre at 10° C. will occupy at 0° C., we find

$$\frac{1}{(1 + 10 \times 0{\cdot}003665)} = 0{\cdot}965$$

How much space do 103·665 cubic centimetres at 10° C. occupy at 0° C.?

$$\frac{103{\cdot}665}{1 + (10 \times 0{\cdot}003665)} = 100.$$

The general rule of these calculations may be briefly expressed as follows:—

To calculate the volume of a gas from a lower to a higher temperature, we have in the first place to find the expansion for the volume unit, which is done by adding to 1 the product of the multiplication of the thermometrical difference by 0·003665; and then to multiply the product of this calculation by the number of volume units found in the analytical process. On the other hand, to reduce the volume of a gas from a higher to a lower temperature, we have to divide the number of volume units found in the analytical process, by the product of the multiplication of the thermometrical difference by 0·003665.

β. Reduction of the Volume of a Gas of a certain given Density to 760 *Millimetres Barometric Pressure, or any other given Pressure.*

According to the law of *Mariotte*, the volume of a gas is inversely as the pressure to which it is exposed; or, in other words, a gas occupies the greater space the less the pressure upon it, and the less space the greater the pressure upon its surface.

Thus, supposing a gas to occupy a space of 10 cubic centimetres, at a pressure of 1 atmosphere, it will occupy 1 cubic centimetre at a pressure of 10 atmospheres, and 100 cubic centimetres at a pressure of $\frac{1}{10}$ atmosphere.

Nothing, therefore, can be more easy than the reduction of a gas of a certain given tension to 760 millimetres bar. pressure, or any other given pressure, *e.g.*, 1000 millimetres, which is frequently used in the analysis of gases.

Supposing a gas to occupy 100 cubic centimetres at 780 millimetres bar., how much space will it occupy at 760 millimetres?

$$760 : 780 :: 100 : x$$
$$x = 102{\cdot}63.$$

How much space will 100 cubic centimetres at 750 millimetres bar. occupy at 760 millimetres?

$$760 : 750 :: 100 : x$$
$$x = 98{\cdot}68.$$

How much space will 150 cubic centimetres at 760 millimetres bar. occupy at 1000 millimetres?

$$1000 : 760 :: 150 : x$$
$$x = 114.$$

γ. Reduction of the Volume of a Gas saturated with Aqueous Vapor, to its actual Volume in the Dry State.

It is a well-known fact that water has a tendency, at all temperatures, to assume the gaseous state. The degree of this tendency (the tension of the aqueous vapor)—which is dependent solely and exclusively upon the temperature, and not upon the circumstance of the water being *in vacuo* or in any gaseous atmosphere—is usually expressed by the height of a column of mercury counterbalancing it. The following table indicates the degrees of tension for the various temperatures at which analyses are likely to be made (compare *Magnus*, "Pogg. Annal.," 61, p. 247).

TABLE.

Temperature in degrees (Centigrade).	Tension of the aqueous vapor expressed in millimetres.	Temperature in degrees (Centigrade).	Tension of the aqueous vapor expressed in millimetres.
0	4·525	21	18·505
1	4·867	22	19·675
2	5·231	23	20·909
3	5·619	24	22·211
4	6·032	25	23·582
5	6·471	26	25·026
6	6·939	27	26·547
7	7·436	28	28·148
8	7·964	29	29·832
9	8·525	30	31·602
10	9·126	31	33·464
11	9·751	32	35·419
12	10·421	33	37·473
13	11·130	34	39·630
14	11·882	35	41·893
15	12·677	36	44·268
16	13·519	37	46·758
17	14·409	38	49·368
18	15·351	39	52·103
19	16·345	40	54·969
20	17·396		

Therefore, if a gas is confined over water, its volume is, *cæteris paribus*, always greater than if it were confined over mercury; since a quantity of aqueous vapor, proportional to the temperature of the water, mixes with the gas, and the tension of this partly counterbalances the column of air that presses upon the gas, and to that extent neutralizes the pressure. To ascertain the actual pressure upon the gas, we must therefore subtract from the apparent pressure so much as is neutralized by the tension of the aqueous vapor.

Suppose we had found a gas to measure 100 cubic centimetres at 759 millimetres bar., the temperature of the confining water being 15° C.: how much space would this volume of gas occupy in the dry state and at 760 millimetres of the barometer?

Our table gives the tension of aqueous vapor at 15° C. = 12·677, the gas is consequently not under the apparent pressure of 759 millimetres, but under the actual pressure of $759 - 12{\cdot}677 = 746{\cdot}323$ mm.

The calculation is now very simple; it proceeds upon the formula given sub β, viz.,

$$760 : 746{\cdot}323 :: 100 : x$$
$$x = 98{\cdot}20.$$

When the volume of a gas has thus been adjusted by the calculations in a and β, or γ, to the thermometrical and barometrical conditions on which the data of Table V. are based, the proportion of it contained in 100 parts by weight of the analysed substance may now be readily calculated by substituting the weight for the volume, and proceeding by simple rule of three.

How many parts of nitrogen are contained in 100 parts of analysed substance, of which 0·5 grm. have yielded 30 cubic centimetres of dry nitrogen gas at 0° C., and 760 millimetres bar.?

In Table V. we find that 1 litre (1000 c.c.) of nitrogen gas at 0° C., and 760 millimetres bar., weighs 1·25456 grm.

We say accordingly:

$$1000 : 1{\cdot}25456 :: 30 : x$$
$$x = 0{\cdot}0376.$$

And then:

$$5 : 0{\cdot}0376 :: 100 : x$$
$$x = 7{\cdot}52.$$

The analysed substance contains consequently 7·52 per cent. by weight of nitrogen.

2. *Calculation of the per-centage Results by Weight, in Cases where the Substance has been separated in Combination with another, or where a Compound has to be determined from one of its Constituents.*

§ 199.

If the body to be determined has not been weighed or measured in its own form, but in some other form or combination, *e.g.*, carbonic acid as carbonate of lime, sulphur as sulphate of baryta, ammonia as nitrogen, chlorine by a graduated solution of iodine, &c., its quantity must first be estimated from that of the compound found before the calculation described in 1 can be made.

This may be accomplished either by rule of three or by some abridged method.

Suppose we have weighed hydrogen in the form of water, and have found 1 grm. of water: how much hydrogen does this contain?

An equivalent of water consists of:

1 of hydrogen
8 of oxygen
9 water.

We say accordingly:

$$9 : 1 :: 1 : x$$
$$x = 0{\cdot}\dot{1}\dot{1}\dot{1}\dot{1}\dot{1}.$$

From this formula results the following equation:

$$\frac{1}{9} \times 1 = x.$$

i.e.

$$0{\cdot}\dot{1}\dot{1}\dot{1}\dot{1}\dot{1} \times 1 = x.$$

Or expressed in general terms:

$$\textit{Water} \times 0{\cdot}11111 = \textit{Hydrogen}.$$

Example.—

517 of water; how much hydrogen?
$517 \times 0{\cdot}11111 = 57{\cdot}444.$

The following equation results also from the above given formula:

$$\frac{9}{1} = \frac{1}{x}$$

$$\text{consequently } 9 = \frac{1}{x}$$

$$\text{consequently } x = \frac{1}{9}:$$

Or, expressed in general terms,

$$\textit{Water divided by } 9 = \textit{Hydrogen}.$$

Example.—

517 of water, how much hydrogen?

$$\frac{517}{9} = 57{\cdot}444$$

In this manner we may find for every compound constant numbers by which to multiply or divide the compound, in order to find the percentage proportion by weight of the constituent sought (compare Table III*).

Thus, for instance, the nitrogen may be estimated from the double bichloride of platinum and chloride of ammonium, by dividing the weight of the latter by 15·96, or multiplying it by 0·06269; thus the carbon may be estimated from the carbonic acid by multiplying the weight of the latter by $0{\cdot}27\dot{2}7$, or dividing it by $3{\cdot}66\dot{6}6$.

These numbers are by no means so simple, convenient, and easy to remember as the number of hydrogen. It is therefore advisable, in the case of carbonic acid, for instance, to fix upon another general term, viz.,

$$\frac{\text{Carbonic acid} \times 3}{11} = \text{Carbon};$$

which is derived from the proportion

$$22 : 6 :: \text{the carbonic acid found} : x$$

Since $\quad 22 : 6 :: 11 : 3$

The object in view may also be attained in a very simple manner, by reference to Table IV.,* which gives the amount of the constituent sought for every number of the compound found, from 1—9; the operator need, therefore, simply add the several values together.

As regards hydrogen, for instance, we find:—

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* See Tables at the end of the volume.

TABLE.

Found.	Sought.	1	2	3	4	5	6	7	8	9
water	hydrogen	0·11111	0·22222	0·33333	0·44444	0·55555	0·66667	0·77778	0·88889	1·00000

From this table it is seen that 1 part of water contains 0·11111 of hydrogen, that 5 parts of water contain 0·55555 of hydrogen; 9 parts, 1·00000, &c.

Now if we wish to know, for instance, how much hydrogen is contained in 5·17 parts of water, we find this by adding the values for 5 parts, for $\frac{1}{10}$ part, and for $\frac{7}{100}$ parts, viz.:—

$$\begin{array}{l} 0\cdot55555 \\ 0\cdot011111 \\ 0\cdot0077778 \\ \hline 0\cdot5744388 \end{array}$$

Why the numbers are to be placed in this manner, and not as follows,

$$\begin{array}{l} 0\cdot55555 \\ 0\cdot11111 \\ 0\cdot77778 \\ \hline 1\cdot44444 \end{array}$$

is self-evident, since arranging them in the latter way would be adding the values for 5, for 1, and for 7 (5 + 1 + 7 = 13) and not for 5·17. This reflection shows also that, to find the amount of hydrogen contained in 517 parts of water, the points must be transposed as follows:—

$$\begin{array}{r@{\cdot}l} 55&555 \\ 1&1111 \\ 0&77778 \\ \hline 57&44388 \end{array}$$

3. *Calculation of the Per-centage Results of Indirect Analyses in Parts by Weight.*

§ 200.

The import of the term "*indirect analysis*," as defined in § 151, shows sufficiently that no universally applicable rules can be laid down for the calculations which have to be made in indirect analyses. The selection of the right way must be left in every individual case to the intelligence of the operator. I will give here the mode of calculating the results in two of the indirect analyses described in Section V. They may serve as examples for other similar calculations.

a. Indirect Determination of Soda and Potassa.

This is effected by determining either the sum total of the sulphated alkalies, and the sulphuric acid contained in them, or the sum total of the chlorides, and the chlorine contained in them.

The calculations may be made in several different ways, of which I will give two:—

a. Suppose we have found 1·976 grm. of sulphate of soda + sulphate of potassa, and in this amount 1 grm. of sulphuric acid: how much potassa is present, and how much soda?

First Method.

If the sulphuric acid = 1 grm. were combined with potassa alone, the quantity of sulphate would amount to 2·17775, according to the proportion:—

$$40 : 87{\cdot}11 :: 1 : x;\ x = 2{\cdot}17775$$

The difference between this number and the weight of mixed sulphate found, *i.e.*, 2·17775–1·9761 = 0·20165, is owing to part of the sulphuric acid in the mixture being combined with soda instead of potassa. The part of sulphate of soda contained in the mixture in the place of sulphate of potassa, is proportional to the difference found; it is calculated as follows:—

The difference between the equivalent of KO, SO_3, and the equivalent of NaO, SO_3 (16·11), is to the equivalent of sulphate of soda (71), as the difference found to the NaO, SO_3 contained in the mixture; or, expressed in numbers—

$$16{\cdot}11 : 71 :: 0{\cdot}20165 : x$$
$$x = 0{\cdot}8887 \quad = NaO, SO_3$$
and
$$1{\cdot}9761 - 0{\cdot}8887 = 1{\cdot}0874 \quad = KO, SO_3$$

From this the following short rule is derived:—

Multiply the sulphuric acid found by 2·17775, deduct from the product the sum of the sulphates, and multiply the difference by 4·4072; the product expresses the quantity of the sulphate of soda.

Second Method.

Expressing sulphate of potassa by K, and sulphate of soda by N, we have the following equation:—

$$K + N = 1{\cdot}9761$$
$$\text{or } K \quad = 1{\cdot}9761 - N$$

1 part of sulphate of soda contains 0·56338; 1 part of sulphate of potassa 0·45919 of sulphuric acid.

The amount of sulphuric acid present in the mixture of sulphate of soda and sulphate of potassa, viz., 1 grm., must consequently be = 0·56338 × the number of units present of sulphate of soda (*i.e.* × the quantity of the sulphate of soda present) + 0·45919 × the number of units present of sulphate of potassa (*i.e.* × the quantity of the sulphate of potassa present).

This gives us the second equation:—

$$(K \times 0{\cdot}45919) + (N \times 0{\cdot}56338) = 1$$
$$\text{Or, } K = \frac{1 - (N \times 0{\cdot}56338)}{0{\cdot}45919}$$

Substituting for K its value according to the first equation, we obtain

$$1{\cdot}9761 - N = \frac{1 - (N \times 0{\cdot}56338}{0{\cdot}45919}$$

and, taking off the denominator of the fraction,

$$(1{\cdot}9761 \times 0{\cdot}45919) - (N \times 0{\cdot}45919) = 1 - (N \times 0{\cdot}56338),$$

that is,

$$0{\cdot}90741 - (N \times 0{\cdot}45919) = 1 - (N \times 0{\cdot}56338).$$

Placing now the two N on one side, we obtain

$$(N \times 0{\cdot}56338) - (N \times 0{\cdot}45919) = 1 - 0{\cdot}90741,$$

or,

$$N = \frac{1 - 0{\cdot}90741}{0{\cdot}56338 - 0{\cdot}45919} = \frac{0{\cdot}09259}{0{\cdot}10419} = 0{\cdot}8887$$

The analysed mixture therefore contains 0·8887 of sulphate of soda, and consequently

$$1{\cdot}9761 - 0{\cdot}8887 = 1{\cdot}0874$$

of sulphate of potassa.

The following general formula may be deduced from the above calculation:—Assuming A to stand for the mixture, and N for the $Na\,O, S\,O_3$, K for the $K\,O, S\,O_3$, and S for the $S\,O_3$, contained in it:

$$N = \frac{S - (A \times 0{\cdot}45919}{0{\cdot}10419}$$

$$\text{and } K = A - N.$$

Suppose we have found 20 grammes of sulphate of potassa + sulphate of soda, and in these 20 grammes 10·5 grammes of sulphuric acid, how much sulphate of potassa does the mixture contain, and how much sulphate of soda?

$$N = \frac{10{\cdot}5 - (20 \times 0{\cdot}45919)}{0{\cdot}10419}, \text{ that is}$$

$$= \frac{10{\cdot}5 - 9{\cdot}1833}{0{\cdot}10419} = \frac{1{\cdot}3162}{0{\cdot}10419} = 12{\cdot}63$$

$$K = 20 - 12{\cdot}63 = 7{\cdot}37.$$

The 20 grammes of the mixture consist accordingly of 12·63 $Na\,O, S\,O_3$, and 7·37 $K\,O, S\,O_3$.

β. Suppose we have found 3 grammes of chloride of sodium and chloride of potassium, and in these 3 grammes 1·6888 of chlorine.

$$\begin{array}{ccccc} \text{Equ. of Chlorine.} & & \text{Equ. of K Cl.} & & \text{Chlorine found.} \\ 35{\cdot}46 & : & 74{\cdot}57 & :: & 1{\cdot}6888 : x \\ & & x & = & 3{\cdot}5514 \end{array}$$

If all the chlorine present were combined with potassium, the weight of the chloride would amount to 3·5514. As the chloride weighs less, chloride of sodium is present, and this in a quantity proportional to the difference, *i. e.*, 3·5514—3 = 0·5514, which is calculated by the following proportion:

The difference between the equivalent of K Cl and the equivalent of NaCl (16·11) is to the equivalent of NaCl (58·46), as the difference found to the chloride of sodium present; or, expressed in numbers:

$$16{\cdot}11 : 58{\cdot}46 :: 0{\cdot}5514 : x$$

$$x = 2 \text{ Na Cl}$$

$$\text{and } 3 - 2 = 1 \text{ K Cl.}$$

From this the following short rule is derived:

Multiply the quantity of chlorine in the mixture by 2·1029, deduct from the product the sum of the chlorides, and multiply the difference by 0·36288; the product expresses the quantity of chloride of sodium contained in the mixed chloride.

The following formulæ will serve to find the sodium and potassium by direct calculation :—

Let x stand for potassium, y for sodium, S for the mixed chloride, A for the chlorine found.

$$x = \frac{[(S-A).\quad 1{\cdot}54] - A}{0{\cdot}63}$$

$$y = \frac{A - [(S-A).\ 0{\cdot}91]}{0{\cdot}63}$$

$$1{\cdot}64 = \frac{Cl}{Na}$$

$$0.91 = \frac{Cl}{K}$$

$$0{\cdot}63 = \frac{Cl}{Na} - \frac{Cl}{K}$$

b. Indirect Determination of Strontia and Lime.

This may be effected by determining the sum total of the carbonates, and the carbonic acid contained in them (§ 154,6). Suppose we have found 2 grammes of mixed carbonate, and in these 2 grammes 0·7386 of carbonic acid.

$$\begin{array}{ccccc} \text{Equ. of } CO_2 & & \text{Equ. of } SrO,\ CO_2 & & CO_2 \text{ found.} \\ 22 & : & 73{\cdot}67 & :: & 0{\cdot}7386 : x \\ & & x & = & 2{\cdot}47335 \end{array}$$

If, therefore, the whole of the carbonic acid were combined with strontia, the weight of the carbonate would amount to 2·47335 grms. The deficiency, = 0·47335, is proportional to the carbonate of lime present, which is calculated as follows :—

The difference between the equivalent of $SrO,\ CO_2$, and the equivalent of $CaO,\ CO_2$ (23·67) is to the equivalent of $CaO,\ CO_2$ (50), as the difference found to the carbonate of lime contained in the mixed salt; or, expressed in numbers :—

$$23{\cdot}67 : 50 :: 0{\cdot}47335 : x$$

$$x = 1$$

The mixture, therefore, consists of 1 gramme of carbonate of lime and 1 gramme of carbonate of strontia. From this the following short rule is derived :—

Multiply the carbonic acid found by 3·3487, deduct from the product the sum of the carbonates, and multiply the difference by 2·1125; the product expresses the quantity of the carbonate of line.

c. Indirect Determination of Chlorine and Bromine (§ 169,1).

Let us suppose the mixture of chloride and bromide of silver to have weighed 2 grammes, and the diminution of weight consequent upon the transmission of chlorine to have amounted to 1 gramme. How much chlorine is there in the mixed salt, and how much bromine?

The decrease of weight here is simply the difference between the weight of the bromide of silver originally present, and that of the chloride of silver which has replaced it; if this is borne in mind, it is easy to understand the calculation which follows:

The difference between the equivalents of bromide of silver and chloride of silver is to the equivalent of bromide of silver as the ascertained decrease of weight is to *x*, *i.e.*, to the bromide of silver originally present in the mixture; or, expressed in numbers:—

$$44{\cdot}507 : 187{\cdot}942 :: 0{\cdot}1 : x$$
$$x = 0{\cdot}42227.$$

The 2 grammes of the mixture therefore contained 0·42227 grm. of bromide of silver, and consequently 2 – 0·42227 = 1·57773 grm. of chloride of silver.

It results from this calculation, that we need simply multiply the ascertained decrease of weight by

$$\frac{187{\cdot}942}{44{\cdot}507} \text{ i.e. with } 4{\cdot}2227$$

to find the amount of bromide of silver originally present in the analysed mixture. And if we know this, we also know of course the amount of the chloride of silver; and from these data we deduce the quantities of chlorine and bromine, as directed in 2, and the proportions of these two substances contained in 100 parts by weight of the analysed compound, as directed in 1.

SUPPLEMENT TO I.

MEAN VALUE, DEFICIENCY, AND EXCESS IN ANALYSES.

§ 201.

If, in the analysis of a substance, one of the constituents is estimated from the loss, or, in other words, by subtracting from the original weight of the analysed substance the ascertained united weight of the other constituents, it is evident that in the subsequent per-centage calculation the sum total must invariably be 100. Every loss suffered or excess obtained in the determination of the several constituents will, of course, fall exclusively upon the one constituent which is estimated from the loss. It is evident, therefore, that quantitative estimations of this kind can afford no guarantee of correctness, unless the other constituents have been determined by good methods, and with the greatest care. The accuracy of the results will of course be the greater, the less the number of constituents determined in the direct way.

If, on the other hand, every constituent of the analysed compound has been determined separately, it is obvious that, were the results absolutely accurate, the united weight of the several constituents must be exactly equal to the original weight of the analysed substance. Since, however, as we have seen in § 96, certain inaccuracies attach to every analysis, without exception, the sum total of the results in the per-centage calculation will sometimes exceed, and at others fall short of, 100.

In all cases of this description, the only proper way is to give the results as actually found.

So, for instance, *Pelouze* found, in his analysis of chromate of chloride of potassium,

Potassium	21·88
Chlorine	19·41
Chromic acid	58·21
	99·50

Berzelius, in his analysis of sesquioxide of uranium and potassa,

Potassa	12·8
Sesquioxide of uranium	86·8
	99·6

Plattner, in his analysis of magnetic iron pyrites.

	Of Fahlun.	*Of Brasil.*
Iron	59·72	59·64
Sulphur	40·22	40·43
	99·94	100·07

It is altogether inadmissible to distribute any chance deficiency or excess, proportionally among the several constituents of the analysed compound, as such deficiency or excess of course never arises from the several estimations in the same measure; moreover, such a way of arranging the calculation of the results deprives other chemists of the power of judging of the accuracy of the analysis. No one need be ashamed to confess having obtained somewhat too little or somewhat too much in an analysis, provided, of course, the deficiency or excess be confined within certain limits, which differ in different analyses, and which the experienced chemist always knows how to fix properly.

In cases where an analysis has been made twice, or several times, it is usual to take the arithmetical mean as the correct result. It is obvious that an average of the kind deserves the greater confidence the less the results of the several analyses differ. The results of the several analyses must, however, also be given, or, at all events, the maximum and minimum.

Since the accuracy of an analysis is not dependent upon the quantity of substance subjected to the analytical process (provided always this quantity be not altogether too small), the average of the results of several analyses is to be taken quite independently of the quantities used; in other words, you must not add together the quantities used, on the one hand, and the weights obtained in the several analyses on the other, and deduce from these data the per-centage amount; but you must calculate the latter from the results of each analysis separately, and then take the arithmetical mean of the numbers so obtained.

Suppose a substance, which we will call AB, contains fifty per cent. of A; and suppose two analyses of this substance have given the following results:—

1) 2 grammes of AB have given 0·99 grm. of A.
2) 50 „ „ 24·00 „

From analysis

No. 1, it results that AB contains 49·50 per cent. of A.
No. 2, „ „ 48·00 „

Total	97·50
Mean	48·75

It would be quite erroneous to say

$$2 + 50 = 52 \text{ of AB gave } 0{\cdot}99 + 24{\cdot}00 = 24{\cdot}99 \text{ of A,}$$

therefore 100 of AB. contain 48·06 of A ;
for it will be readily seen that this way of calculating destroys nearly altogether the influence of the more accurate analysis of the two (1) upon the average, on account of the proportionally small amount of substance used in that analysis.

II. Deduction of Empirical Formulæ.

§ 202.

If the per-centage composition of a substance is known, a so-called *empirical* formula may be deduced from this; in other words, the relative proportion of the several constituents may be expressed in equivalents—in a formula which, upon recalculation in per-cents will give numbers corresponding perfectly, or nearly, with those obtained by the analysis of the substance in question. We are compelled to confine ourselves to the expression of empirical formulæ, in the case of all substances of which we cannot determine the equivalent, as *e.g.*, mannite, woody fibre, mixed substances, &c.

The method of deducing empirical formulæ is very simple, and will be readily understood from the following reflections :—

How should we proceed to find the relative number of equivalents in carbonic acid?

We should say :—

The equivalent of the oxygen is to the amount of oxygen in the equivalent of carbonic acid, as 1 is to x, *i.e.*, to the number of equivalents of oxygen contained in carbonic acid ; accordingly

$$8 : 16 :: 1 : x$$
$$x = 2.$$

In the same manner we should find the number of equivalents of carbon present in carbonic acid, by the following proportion :—

$$\underset{\text{(equivalent of carbon)}}{6} : \underset{\text{(carbon in one equivalent of carbonic acid.)}}{6} :: 1 : x$$
$$x = 1.$$

Now let us suppose we did not know the equivalent of carbonic acid, but simply its per-centage composition, viz.,

27·273	of carbon.
72·727	of oxygen
100·000	of carbonic acid,

the relative proportion of the equivalents might still be ascertained, even though any other given number, say 100, be selected for the equivalent of carbonic acid. Let us suppose we adopt 100 as the equivalent of carbonic acid; thus,

8 : 72·727 :: 1 : x
(Equ. of O) (Amount of oxygen in the assumed equivalent of 100)
$x = 9·0910$

and

6 : 27·273 :: 1 : x
(Equ. of C) (Amount of carbon in the assumed equivalent of 100)
$x = 4·5455.$

We see here that although the *numbers* which express the relative proportion of the atoms of oxygen and carbon, have changed, yet the *relative proportion* remains the same; since

$$4·5455 : 9·0910 :: 1 : 2.$$

The process may accordingly be expressed in general terms as follows: Assume any number, say 100 (because this is the most convenient), as the equivalent of the compound for which you wish to establish an empirical formula, and ascertain how often the equivalent of each constituent severally is contained in the amount of the same constituent resulting from the analysis. When you have thus found the numbers expressing the relative proportion which the several constituents bear to each other, you have attained your purpose—viz., the deduction of an empirical formula. Still, it is usual to reduce the numbers found to the simplest expression.

Now let us take a somewhat complicated case, *e.g.*, the deduction of the empirical formula for mannite.

The per-centage composition of mannite is

39·56 of carbon
7·69 of hydrogen
52·75 of oxygen
100·00

This gives the following proportions:

$6 : 39·56 :: 1 : x$
$x = 6·593$
$1 : 7·69 = 1 : x$
$x = 7·690$
$8 : 52·75 = 1 : x$
$x = 6·593$

We have now the empirical formula for mannite, viz.,

$$C_{6·593} \qquad H_{7·690} \qquad O_{6·593}$$

A glance shows that the number of the equivalents of the carbon is equal to that of the equivalents of the oxygen; and the question is now whether the relative proportion found may not be expressed by smaller numbers.

A simple calculation suffices to answer this question, viz.,

$$6{\cdot}593 : 7{\cdot}690 :: 60 : x$$

(Any other number might be substituted for 60, as the third term of the proportion, but 60 is the most convenient, since it is divisible without remainder by most of the numbers.)

$$x = 70$$

We have accordingly now the simple formula,

$$C_{60} \quad H_{70} \quad O_{60} = C_6 \quad H_7 \quad O_6.$$

The per-centage composition of mannite given above having been deduced from the results of actual analyses, the correctness of the formula derived from it cannot be called in question. Now let us take the results of a direct analysis of mannite.

Oppermann obtained, upon the combustion of 1·593 grm. of mannite, with oxide of copper, 2·296 grammes of carbonic acid and 1·106 grm. of water. This gives by calculation in per-cents.

39·31	of carbon
7·71	of hydrogen
52·98	of oxygen
100·00	

which, calculated as above, gives

$$C_{6{\cdot}552} \qquad H_{7{\cdot}710} \qquad O_{6{\cdot}622}$$

as the first expression of the empirical formula; and by the proportion:

$$6{\cdot}552 : 7{\cdot}710 :: 6 : x$$
$$x = 7{\cdot}06$$

A glance at these numbers shows that 7·06 may be properly exchanged for 7, and also that the difference between 6·552 and 6·622 is so trifling that both may be expressed by the same number. These considerations lead therefore likewise to the formula

$$C_6 \quad H_7 \quad O_6$$

The proof whether the formula is correct or not is obtained by its recalculation in per-cents. The less the calculated per-centage differs from that found, the more reason there is to believe in the correctness of the empirical formula. If the difference is more considerable than can be accounted for by the defects inherent in the methods, there is every reason to believe the formula fallacious, in which case it is necessary to establish a more correct one; for it will be readily seen that, in the case of substances of which the equivalent is not known, different formulæ may be deduced from one and the same analysis, or from several very nearly corresponding analyses; since the numbers found are never absolutely correct, but only approximate.

Thus, for instance, in the case of mannite:

	Calculated for		for	found
C_6	39·56	C_8	39·67	39·31
H_7	7·69	H_9	7·44	7·71
O_6	52·75	O_8	52·89	52·98
	100·00		100·00	100·00

III. Deduction of Rational Formulæ.

§ 203.

If both the per-centage composition and the equivalent of a substance are known, it is easy to deduce its *rational* formula—that is, a formula expressing not only the relative proportion of the equivalents, but also their absolute number.

The following examples may serve for illustration :—

1. *Deduction of the Rational Formula of Hyposulphuric Acid.*

Analysis has given, in the first place, the per-centage composition of hyposulphuric acid, and, in the second place, the per-centage composition of hyposulphate of potassa, viz.,

Sulphur	44·44	Potassa	39·551
Oxygen	55·56	Hyposulphuric acid . .	60·449
Hyposulphuric acid	100·00	Hyposulphate of potassa	100·000

(Equivalent of potassa = 47·11)

From the proportion :

$$39{\cdot}551 : 60{\cdot}449 :: 47{\cdot}11 : x$$
$$x = 72$$

results, as x, the sum of the equivalents of the constituents contained in hyposulphuric acid—in other terms, the equivalent of hyposulphuric acid.

Having thus ascertained the correct equivalent of hyposulphuric acid, it is unnecessary to assume a hypothetical one, as we were obliged to do in the case of mannite.

Thus we may state at once :

$$100 : 44{\cdot}44 :: 72 : x$$
$$x = 32\,;$$

i. e. like the sum of the equivalents of the sulphur ; and again :

$$100 : 55{\cdot}56 :: 72 : x$$
$$x = 40\,;$$

i. e. like the sum of the equivalents of the oxygen.

Now the equivalent of sulphur, *i. e.* 16, is contained twice in 32 ; and the equivalent of oxygen, *i. e.* 8, is contained five times in 40 ; the rational formula for hyposulphuric acid is accordingly,

$$S_2\,O_5.$$

2. *Deduction of the Rational Formula of Benzoic Acid.*

Stenhouse obtained from 0·3807 grm. of hydrated benzoic acid, dried at 212° F., 0·9575 of carbonic acid and 0·1698 of water.

0·4287 grm. of benzoate of silver, dried at 212° F., gave 0·202 of silver. From these numbers results the following composition :—

Carbon	68·67	Oxide of silver . . .	50·67
Hydrogen	4·95	Benzoic acid	49·33
Oxygen	26·38		
		Benzoate of silver . .	100·00
Hydrated benzoic acid	100·00		

(Equivalent of the oxide of silver = 115·97)

$$50{\cdot}67 : 49{\cdot}33 :: 115{\cdot}97 : x$$
$$x = 112{\cdot}904$$

i. e. the equivalent of anhydrous benzoic acid; the equivalent of the hydrated acid is accordingly $= 112{\cdot}904 + 9 = 121{\cdot}904$; we say therefore now:

$$100 : 68{\cdot}67 :: 121{\cdot}904 : x$$
$$x = 83{\cdot}711$$
$$100 : 4{\cdot}95 :: 121{\cdot}904 : x$$
$$x = 6{\cdot}035$$
$$100 : 26{\cdot}38 :: 121{\cdot}904 : x$$
$$x = 32{\cdot}158$$

6	is contained in	83·711	13·95	times
1	„	6·035	6·03	„
8	„	32·158	4·02	„

A glance at the numbers resulting from these divisions suffices to show that 13·95 may be exchanged for 14, and that 6 may be substituted for 6·03, and 4 for 4·02. The rational formula for the hydrate of benzoic acid is accordingly,

$$C_{14}\ H_6\ O_4.$$

	This gives, by calculation,	The numbers found by *Stenhouse* were,
C	68·85	68·67
H	4·92	4·95
O	26·23	26·38
	100·00	100·00

3. *Deduction of the Rational Formula of Theine.*

Stenhouse's analysis of theine, free from water of crystallization, gave the following results:

1. 0·285 grm. of theine gave 0·5125 of carbonic acid and 0·132 of water.

2. The combustion of theine with oxide of copper gave a gaseous mixture of CO_2 and N, in the proportion of 4 of the former to 1 of the latter.

3. 0·5828 grm. of the double salt of hydrochlorate of theine and bichloride of platinum, gave 0·143 platinum.

From these numbers results the following per-centage composition:—

Carbon . .	49·05
Hydrogen .	5·14
Nitrogen . .	28·61
Oxygen . .	17·20
	100·00

and 196·91 as the equivalent of theine. For there is every reason to suppose that the composition of the double salt of hydrochlorate of theine and bichloride of platinum is

$$\text{Theine} + H\,Cl + Pt\,Cl_2$$

The equivalent of this double salt is found by the following proportion:

$$0{\cdot}143 : 0{\cdot}5828 :: 98{\cdot}94\ (\text{equivalent of platinum}) : x$$
$$x = 403{\cdot}23\,;$$

and consequently the equivalent of theine, by subtracting from 403·23 the sum of 1 equivalent of bichloride of platinum (169·86) and 1 equivalent of hydrochloric acid (36·46)

$$403{\cdot}23-(169{\cdot}86+36{\cdot}46)=196{\cdot}91.$$

This supplies the following proportions :—

$$100 : 49{\cdot}05 :: 196{\cdot}91 : x \qquad x = 96{\cdot}584$$

$$100 : 5{\cdot}14 :: 196{\cdot}91 : x \qquad x = 10{\cdot}121$$

$$100 : 28{\cdot}61 :: 196{\cdot}91 : x \qquad x = 56{\cdot}336$$

$$100 : 17{\cdot}20 :: 196{\cdot}91 : x \qquad x = 33{\cdot}868$$

6	is contained in	96·584,	16·09	times
1	„	10·121,	10·12	„
14	„	56·336,	4·02	„
8	„	33·868,	4·23	„

for which may be substituted 16,—10,—4,—and 4, which gives the following formula :

$$C_{16}\,H_{10}\,N_4\,O_4$$

This gives by calculation,	Found.
49·47	49·05
5·15	5·14
28·89	28·61
16·49	17·20
100·00	100·00

The double hydrochlorate of theine and bichloride of platinum gives platinum in 100 parts,

Calculated.	Found.
24·70	24·53

4. *Special Method of Deducing Rational Formulæ for Oxygen Salts.*

a. In the case of Compounds containing no Isomorphous Constituents.

The rational formulæ for oxygen salts may be deduced also by a method different from the foregoing, viz., by ascertaining the ratio which the respective quantities of oxygen bear to each other. This method is exceedingly simple.

In an analysis of crystallized sulphate of soda and ammonia, I found,

Soda	17·93
Oxide of ammonium .	15·23
Sulphuric acid . .	46·00
Water	20·84
	100·00

31 of $Na\,O$	contain	8 of O,	consequently	17·93 of $Na\,O$	contain	4·63 of O.
26 ... $N\,H_4\,O$	...	8 ... O,	...	15·23 ... $N\,H_4\,O$	...	4·68 ... O.
40 ... $S\,O_3$	...	24 ... O,	...	46·00 ... $S\,O_3$	...	27·60 ... O.
9 ... $H\,O$	...	8 ... O,	...	20·84 ... $H\,O$	...	18·52 ... O.

The respective quantities of oxygen,

4·63 : 4·68 : 27·60 : 18·52,

stand to each other in the same ratio

as 1 : 1·01 : 5·97 : 4·00,

for which we may safely substitute

1 : 1 : 6 : 4,

which leads to the formula

$$\text{Na O, N H}_4\text{ O, 2 S O}_3 + 4\text{ H O}$$
$$\text{or, Na O, S O}_3 + \text{N H}_4\text{ O, S O}_3 + 4\text{ Aq.}$$

b. In the case of Compounds containing Isomorphous Constituents. It is a well-known fact that isomorphous constituents may replace each other in all proportions; therefore, in establishing a formula for compounds containing isomorphous constituents, the latter are taken *collectively*; that is, they are expressed in the formula as *one and the same* body. This very frequently occurs in the calculation of formulæ for minerals.

A. Erdmann found in *Monradite*

			Amount of Oxygen.
Silicic acid	56·17		29·179
Magnesia	31·63	12·652	14·601
Protoxide of iron	8·56	1·949	
Water	4·04		3·590
	100·40		

Now the ratio between

3·59 : 14·601 : 29·179
is as 1 : 4·07 : 8·1,

for which we may safely substitute

1 : 4 : 8.

Designating 1 equivalent of metal by R, we obtain from these numbers the formula:—

$$4\text{ (R O, Si O}_2\text{)} + \text{HO or } 4 \left\{\begin{matrix}\text{Mg}\\ \text{Fe}\end{matrix}\right\} \text{O, Si O}_2\text{)} + \text{Aq.}$$

Besides isomorphous substances, all bodies of analogous composition possess the faculty of replacing each other in compounds; thus we find that KO, Na O, Ca O, Mg O, &c., replace each other. These substances likewise must be expressed collectively in the formula.

Abich found in *Andesine*

			Amount of Oxygen.
Silicic acid	59·60		30·94
Alumina	24·28	11·22	11·70
Sesquioxide of iron	1·58	0·48	
Lime	5·77	1·61	3·90
Magnesia	1·08	0·43	
Soda	6·53	1·68	
Potassa	1·08	0·18	
	99·92		

The ratio between 3·90 : 11·70 : 30·94

is as 1 : 3 : 7·93 ;

for which we may safely substitute

1 : 3 : 8.

Designating 1 equivalent of metal by R, we obtain from these numbers the formula :—

$$\begin{aligned} & R\,O + R_2\,O_3 + 4\,Si\,O_2 \\ = {} & R\,O,\,Si\,O_2 + R_2\,O_3,\,3\,Si\,O_2, \end{aligned}$$

which may likewise be written :

$$\left.\begin{matrix} Ca \\ Mg \\ Na \\ K \end{matrix}\right\} O,\,Si\,O_2 + \left.\begin{matrix} Al_2 \\ Fe_2 \end{matrix}\right\} O_3,\ 3\,Si\,O_2.$$

Showing thus that this mineral is *Leucite* ($K\,O,\,Si\,O_2 + Al_2\,O_3, 3\,Si\,O_2$), in which the greater part of the potassa is replaced by lime, soda, and magnesia, and a portion of the alumina by sesquioxide of iron.

These remarks respecting the deduction of formulæ for oxygen salts, apply of course equally to metallic sulphides.

IV. Calculation of the Density of the Vapors of Volatile Bodies, and Application of the Results, as a Means of controlling their Analyses, and determining their Equivalents.

§ 204.

The specific gravity of a compound gas is equal to the sum of the specific gravities of its constituents in one volume.

E.g., 2 volumes of hydrogen gas and 1 volume of oxygen gas give 2 volumes of aqueous vapor. If they gave simply 1 volume of aqueous vapor, the specific gravity of the latter would be equal to the sum total of the specific gravity of the oxygen and double the specific gravity of the hydrogen—viz.,

$$\begin{array}{r} 2 \times 0{\cdot}0693 = 0{\cdot}1386 \\ +\,1{\cdot}1083 \\ \hline =1{\cdot}2469 \end{array}$$

But as they give 2 volumes of aqueous vapor, these 1·2469 are distributed between the 2 volumes; accordingly

$$\frac{1{\cdot}2469}{2} = 0{\cdot}62345$$

It will be readily seen that the knowledge of the density of the vapor of a compound supplies an excellent means of controlling the correctness of the relative proportions of the equivalents assumed in a formula, provided the density has been determined at a temperature, at least 54–72° F., above the boiling point of the analysed substance; as it is only under these conditions that the actual and constant density of the vapor can be ascertained.

For instance: from the results of the ultimate analysis of camphor, has been deduced the empirical formula:

$$C_{10}H_8O.$$

Dumas found the density of the vapor of camphor = 5·312. Now, by what means do we find whether this formula is correct with respect to the relative proportions of the equivalents?

Specific gravity of the vapor of carbon	0·831
„ „ hydrogen gas	0·0693
„ „ oxygen gas	1·108

$$\begin{array}{rlrl} 10 \text{ equ. } C = 10 \text{ volumes} & = 10 \times 0{\cdot}831 & = & 8{\cdot}310 \\ 8 \text{ equ. } H = 16 \text{ volumes} & = 16 \times 0{\cdot}0693 & = & 1{\cdot}109 \\ 1 \text{ equ. } O = 1 \text{ volume} & = 1 \times 1{\cdot}108 & = & 1{\cdot}108 \\ \hline & & & 10{\cdot}527 \end{array}$$

This sum is almost exactly twice as large as the specific gravity found by direct experiment ($\frac{10{\cdot}527}{2} = 5{\cdot}263$); which shows that the relative proportions of the equivalents are correctly given in the empirical formula of camphor. But whether the formula is correct, also, with regard to the absolute number of equivalents, cannot be determined simply from the density of the vapor, because we do not know to how many volumes of camphor vapor 1 equivalent of camphor corresponds. *Liebig* assumes the equivalent of camphor to correspond to 2 volumes, and gives accordingly the formula $C_{10}H_8O$; whilst *Dumas* assumes it to correspond to 4 volumes, and gives the formula accordingly $C_{20}H_{16}O_2$.

The knowledge of the density of the vapor affords, therefore, in reality, simply a means of controlling the correctness of the analysis, but not of establishing a rational formula; and although it is made to serve sometimes for the latter purpose, yet this can be done only in the case of substances for which we are able to infer from analogy a certain ratio of condensation: thus, for instance, experience proves that 1 equivalent of most of the hydrates of the volatile organic acids, of alcohols, &c., corresponds to 4 volumes.

In § 203, 2, we have deduced the rational formula of hydrated benzoic acid at $C_{14}H_6O_4$. *Dumas* and *Mitscherlich* found the density of the vapor of this acid = 4·26.

Now nearly the same number is obtained by dividing by 4 the sum total of the specific gravities of the several constituents contained in 1 equivalent of hydrated benzoic acid, viz.,

$$\begin{array}{rr} 14 \text{ volumes } C = & 11{\cdot}634 \\ 12 \text{ volumes } H = & 0{\cdot}831 \\ 4 \text{ volumes } O = & 4{\cdot}432 \\ \hline & 16{\cdot}897 \end{array}$$

$$\frac{16{\cdot}897}{4} = 4{\cdot}224$$

Hermann Kopp ("Compt. rend.," 44, 1347; "Chem. Centralbl.," 1857, 595,) has recently called attention to the fact that, if the equivalent of a substance is calculated upon H = 1, and the density of the vapor of the same upon atmospheric air = 1, the division of the equivalent by the density of the vapor gives the following quotients, 28·88 14·44 7·22

according as the formula corresponds to 4, 2, or 1 volume of vapor:

28·88 corresponds to a condensation to 4 volumes
14·44 " " " 2 "
7·22 " " " 1 volume

Kopp calls these numbers *normal quotients.* If the density of the vapor is not quite exact, but only approximate (determined by experiment), other numbers are found, but, to be correct, these must come near the normal numbers.

If, therefore, we know the equivalent of a body, we may, with the greatest facility, ascertain whether the determination of the density of the vapor of the body has given approximately correct results or not.

Gay-Lussac found the density of the vapor of ethyl-alcohol = 1·6133; *Dalton* = 2·1 (*Gmelin's* "Handbuch der Chemie," 4, 550).

Now, which is the correct number?

The equivalent of alcohol, $C_4H_6O_2$, is 46.

$$\frac{46}{2{\cdot}1} = 21{\cdot}9$$

$$\frac{46}{1{\cdot}6133} = 28{\cdot}5$$

It is evident that *Gay-Lussac's* number is approximately correct, for the quotient found by it comes very near the normal quotient, 28·88.

Again, if we know the equivalent of a body, and the number of volumes of vapor corresponding to 1 equivalent, we may also, with the same facility, theoretically calculate the density of the vapor of the body. For instance: the equivalent of hydrated benzoic acid is 122. The division of this number by 28·88 gives 4·224, as the density of the vapor, which is the same as that found by actual experiment.

And, lastly, if we approximately know (by experiment) the density of the vapor of a body, and also the ratio of condensation, we may, with the aid of these quotients, approximately calculate the equivalent of the body.

E.g. The density of the vapor of acetic ether has been found = 3·112. The multiplication of this number by 28·88 gives 89·87 as the equivalent of acetic ether, which comes near the actual equivalent, 88.

Having thus shown how the knowledge of the density of the vapor of a body is turned to account as a means of controlling the results of an ultimate analysis of the same, we will now proceed to show how the density of the vapor is calculated from the data obtained as described in § 193.

We will take as an illustration *Dumas's* estimation of the specific gravity of the vapor of camphor.

The results of the process were as follows:—

Temperature of the air		13·5° C.
Barometer		742 millimetres
Temperature of the bath at the moment of sealing the globe		244° C.
Increase of the weight of the globe	0·708 grm.	
Volume of mercury required to fill the globe . . .	295 cubic centimetres	
Residual air	0	

Now, to find the density of the vapor, we have to determine,

1. The weight of the air which the globe holds. (This we must necessarily know for the solution of the second question.)
2. The weight of the camphor vapor which the globe holds.
3. The volume to which the camphor vapor corresponds, at 0° C. and 0·760 millimetres bar.

The solution of these questions is quite simple; and if the calculation, notwithstanding, appears somewhat complicated, this is merely owing to certain reductions and corrections which are required.

1. *The weight of the air in the globe.*

The globe holds 295 cubic centimetres, as we see by the volume of mercury required to fill it.

Now, what is the weight of 295 cubic centimetres of air at 13·5° C. and 0·742 millimetre bar., at 0° C. and 760 millimetres bar.?

The question is solved according to the directions of § 198, by the following proportions:—

$$760 : 742 :: 295 : x$$

$x = 288$ cubic centimetres. (At 13·5° C. and 760 millimetres bar.)

and again:

$$\frac{288}{1 + (13{\cdot}5 \times 0{\cdot}00366)} = \frac{288}{1{\cdot}04941} = 274$$ cubic centimetres (at 0° C. and 760 millimetres bar.)

Now 1 cubic centimetre of air at 0° C. and 760 millimetres bar. weighs 0·00129366 grm.; 274 cubic centimetres weigh accordingly

$$0{\cdot}00129366 \times 274 = 0{\cdot}35446 \text{ grm.}$$

2. *The Weight of the Vapor.*

At the beginning of the experiment we tared the globe + the air within it; we afterwards weighed the globe + the vapor (but without the air);—to find, therefore, the actual weight of the vapor, it is not sufficient to subtract the tare from the weight of the globe filled with vapor, since (*glass* + *vapor*)—(*glass* + *air*) is not = *vapor;* but we have either to subtract, in the first place, the weight of the air from the tare, or to add the weight of the air to the increase of the weight of the globe. Let us do the latter:—

Weight of air in the globe	= 0·35446 grm.
Increase of weight of globe	= 0·70800 grm.
The weight of the vapor is accordingly	= 1·06246 grm.

3. *The Volume to which this Weight of* 1·06246 *grm. of Vapor corresponds at* 0° C. *and* 760 *millimetres bar.*

We know from the above-given data that this weight corresponds to 295 cubic centimetres at 244° C., and 742 millimetres bar. Before we can proceed to reduce this volume according to the directions of § 198, the following corrections are necessary:—

a. 244° C. of the mercurial thermometer correspond, according to *Magnus's* experiments, to 239° C. of the air thermometer (see Table VI).

b. According to *Dulong* and *Petit*, glass expands (commencing at 0° C.) $\frac{1}{35000}$ of its volume for each degree C. The volume of the globe at the moment of sealing was accordingly—

$$295 + \frac{295 \times 239}{35000} = 297 \text{ cubic centimetres.}$$

If we now proceed to reduce this volume upon 0° C. and 760 millimetres bar., we find by the proportion,

$$760 : 742 :: 297 : x$$

x (*i.e.* cubic centimetres of vapor at 760 millimetres bar. and 239° C.)

$= 290$; and by the equation,

$$\frac{290}{1 + (239 \times 0{\cdot}00366)} = x$$

x (*i.e.* cubic centimetres of vapor at 760 millimetres bar., and 0° C.) = 154·6.

154·6 cubic centimetres of camphor vapor at 0° C, and 760 millimetres bar. weigh accordingly 1·06246 grm.

1 litre (1000 cubic centimetres) weighs consequently 6·87231 grms.; since

$$154{\cdot}6 : 1{\cdot}06246 :: 1000 : 6{\cdot}87231.$$

Now 1 litre of air at 0° C. and 760 millimetres bar. weighs 1·29366 grm.

The specific gravity of the camphor vapor consequently is = 5·312; since

$$1{\cdot}29366 : 6{\cdot}87231 :: 1 : 5{\cdot}312.$$

PART II.

SPECIAL PART.

I. ANALYSIS OF WATERS.

A. Analysis of Fresh Water in Springs, Wells, Brooks, Rivers, &c.*

§ 205.

The analysis of the several kinds of fresh water is *usually* restricted to the quantitative estimation of the following substances.

a. Bases: Soda, lime, magnesia.

b. Acids: Sulphuric acid, silicic acid, carbonic acid (combined), chlorine.

c. Mechanically suspended Matters: Clay, &c.

We confine ourselves, therefore, here to the estimation of these bodies. In cases where the examination is to extend to other constituents besides these, the methods given in §§ 206—213 are resorted to.

I. *The Water is clear.*

1. *Determination of the Chlorine.*—This may be effected, either, *a*, by the gravimetric, or, *b*, by the volumetric method.

a. Gravimetric Method.

Take 500—1000 grammes or c.c.† Acidify with nitric acid, and precipitate with nitrate of silver. Filter when the precipitate has *completely* subsided (§ 141, I., *a*). If the quantity of the chlorine is so inconsiderable that the solution of nitrate of silver produces only a slight turbidity, evaporate a larger portion of the water to $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{8}$, &c., of its bulk, filter, wash the precipitate, and treat the filtrate as directed.

b. Volumetric Method.

Evaporate 1000 grammes or c.c. down to a small quantity of residual liquid, and determine the chlorine in this, without previous filtration, by solution of nitrate of silver, with addition of chromate of potassa (§ 141, I., *b*, *a*).

2. *Determination of the Sulphuric Acid.* Take about 1000 grammes or c.c. Acidify with hydrochloric acid and mix with chloride of barium. Filter after the precipitate has *completely* subsided (§ 132, I., 1). If the quantity of the sulphuric acid is very inconsiderable, evaporate the acidified water to $\frac{1}{2}$, $\frac{1}{4}$, $\frac{1}{8}$, &c., of the bulk, before adding the chloride of barium.

3. *Determination of the Silicic Acid, Lime, and Magnesia.*

Evaporate 1000 grammes of the water—best in a platinum dish—after addition of some hydrochloric acid, to dryness, treat the residue with hydrochloric acid and water, filter off from the separated silicic acid, and treat the latter as directed § 140, II., *a*. Estimate the lime and magnesia in the filtrate as directed § 154, 4, *a* (30).

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* Compare the chapter on the same subject in *Fresenius's* "Qualitative Analysis," 5th Edition, § 208.

† As the specific gravity of the fresh water of springs, rivers, &c., differs but little from that of pure water, the several quantities of water may safely be measured instead of weighed. The calculation is facilitated by taking a round number of cubic centimetres.

4. *Determination of the whole Residue and Estimation of the Soda.*

a. Evaporate 1000 grammes or cubic centimetres of the water, with proper care, to dryness, in a platinum or porcelain dish, first over a lamp, finally on the water-bath. Expose the residue, in the air-bath, to a temperature of about 356° F., until no further diminution of weight takes place. This gives the *total amount of the salts*.

b. Treat the residue with water, and add, cautiously, dilute sulphuric acid in moderate excess; cover the vessel during this operation with a dish, to avoid loss from spurting; then place on the water-bath. After ten minutes, rinse the cover by means of a washing bottle, evaporate the contents of the dish to dryness, expel the free sulphuric acid, ignite the residue, in the last stage with addition of some carbonate of ammonia (§ 97, 1), and weigh. The residue consists of sulphate of soda, sulphate of lime, sulphate of magnesia, and some separated silicic acid. It must not redden moist litmus paper. The quantity of the sulphate of soda in the residue is now found by subtracting from the weight of the latter the known weight of the silicic acid and the weight of the sulphate of lime and sulphate of magnesia calculated from the quantities of these earths found in 3.

5. *Direct Estimation of the Soda.*

The soda may also be determined in the direct way, with comparative expedition, by the following method:—

Evaporate 1250 grammes or c.c. of the water, in a dish, to about $\frac{1}{6}$, and then add 2—3 c.c. of thin pure milk of lime, so as to impart a strongly alkaline reaction to the fluid; heat for some time longer, then wash the contents of the dish into a quarter-litre flask. It is not necessary to rinse every particle of the precipitate into the flask; but the whole of the fluid must be transferred to it, and the particles of the precipitate adhering to the dish well washed, and the washings also added to the flask. Allow the contents to cool, dilute to the mark, shake, let deposit, filter through a dry filter, measure off 200 c.c. of the filtrate, corresponding to 1000 grammes of the water, transfer to another quarter-litre flask, mix with carbonate of ammonia and some oxalate of ammonia, add water up to the mark, shake, let deposit, filter through a dry filter, measure off 200 c.c., corresponding to 800 grammes of the water, add some chloride of ammonium,* evaporate, ignite, and weigh the residual chloride of sodium as directed § 98, 3.†

6. Calculate the number found in 1—5 upon 1000 parts of water, and determine from the data obtained the amount of *carbonic acid* in combination, as follows:—

Add together the quantities of sulphuric acid corresponding to the bases found, and subtract from the sum, first, the amount of sulphuric acid precipitated from the water by chloride of barium (2), and, secondly, an amount corresponding to that of the chlorine found (for 1 equivalent of Cl, 1 equivalent of SO_3); the difference expresses the quantity of the carbonic acid combined with the bases in the form of *neutral* carbonates. 40 parts of sulphuric acid remaining after subtracting the quantities just stated, correspond accordingly to 22 parts of carbonic acid. If, by way of control, you wish to determine the combined carbonic acid in the direct way, evaporate 1000 grammes or c. c. of the water, in a flask, until only a small portion is left; add tincture of litmus, then nitric acid of known strength, and proceed as directed § 139, I., *b*, *a*, *bb*.

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* To convert the still remaining sulphate of soda, on ignition, into chloride of sodium.

† This process, which entirely dispenses with washing, presents one source of error—viz., the space occupied by the precipitates is not taken into account. The error resulting from this is, however, so trifling, that it may safely be disregarded, as the excess of weight amounts to 0·2 per cent. at the most.

7. *Control.*

If the quantities of the soda, lime, magnesia, sulphuric acid, silicic acid, carbonic acid, and chlorine are added together, and an amount of oxygen corresponding to the chlorine (since this latter is combined with metal and not with oxide) is subtracted from the sum, the balance remaining must nearly correspond to the total amount of the salts found in 4, *a*. *Perfect* correspondence cannot be expected, since, 1, upon the evaporation of the water chloride of magnesium is partially decomposed, and converted into a basic salt; 2, the silicic acid expels some carbonic acid; 3, it is difficult to free carbonate of magnesia from water without incurring loss of carbonic acid; and, 4, the residue remaining upon the evaporation of the water contains the carbonate of magnesia as a *basic* salt, whereas, in our calculation, we have assumed the quantity of carbonic acid corresponding to the *neutral* salt.

II. *The water is not clear.*

Fill a large flask of known capacity with the water, close with a glass stopper, and allow the flask to stand in the cold until the suspended matter is deposited; draw off the clear water with a siphon as far as practicable, filter from the residual sediment, dry or ignite the contents of the filter, and weigh. Treat the clear water as directed in I.

Respecting the calculation of the analysis, I refer to § 213, remarking simply that it is *usually*[*] arranged upon the following principles:

Chlorine is calculated in combination with the sodium; if there is an excess, this is calculated in combination with the magnesium; if there is still an excess, this is calculated in combination with the calcium. If, on the other hand, there remains an excess of soda, this is calculated in combination with sulphuric acid. The *sulphuric acid*, or, if part of this has been calculated already in combination with soda, the remainder of it, is estimated in combination with lime. The *silicic acid* is put down in the free state, the remainder of the *lime* and the *magnesia* as carbonates, and this, according to circumstances, either as neutral carbonates or as bicarbonates.

It must always be borne in mind that the results of the *qualitative* analysis may render another arrangement of the calculation necessary. In the statement of the results, the quantities are often calculated for 10,000 parts of water instead of 1000 parts; and frequently also in grains per pound of water (1 pound = 7680 grains).

For technical purposes, it is sometimes sufficient to estimate the hardness of the water (the relative amount of lime and magnesia in it) by means of a solution of soap of known strength. A detailed description of this method, which was first employed by *Clark*, has been given by *Fehling* and *Faiszt* (Gewerbeblatt aus Würtemberg, 1852, 193;—"Pharmaceut. Centralbl.," 1852, 513). It is only by strict adherence to the rules there given that accurate and corresponding results are obtained by this method.

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[*] There is a certain latitude allowed in the mode of arranging the results of an analysis.

B. ANALYSIS OF MINERAL WATERS.*

§ 206.

In the analysis of mineral waters we have a larger number of substances than claim our attention in that of fresh waters. In general, the following substances have to be quantitatively determined in the analysis of a mineral water:—

a. Bases: Potassa, soda, lithia, ammonia, lime, baryta, strontia, magnesia, alumina, protoxide of iron, protoxide of manganese (oxide of zinc, protoxide of nickel,† protoxide of cobalt,† oxide of copper, oxide of lead, binoxide of tin, teroxide of antimony).

b. Acids: Sulphuric acid, phosphoric acid, silicic acid, carbonic acid, boracic acid, nitric acid, hyposulphurous acid, chlorine, iodine, bromine, fluorine, hydrosulphuric acid, crenic acid, apocrenic acid, formic acid, propionic acid, &c. (arsenious and arsenic acids, titanic acid†).

c. Non-combined elements and indifferent gases: Oxygen, nitrogen, light carbide of hydrogen.

d. Indifferent organic matters.

Many of these substances occur in most springs, in considerable proportions; of the bases, more particularly soda, lime, magnesia, and sometimes also protoxide of iron; and of the acids,—sulphuric acid, carbonic acid, silicic acid, chlorine, and sometimes also hydrosulphuric acid. The others are almost invariably found only in trifling and often in exceedingly minute proportions. The substances between brackets occur usually only in the muddy, ochreous, or solid sinter deposits,‡ which form, in most mineral springs, in the parts where the air acts upon the water flowing off, or kept in a reservoir.

The subject of the analysis of mineral waters is properly treated under two heads, viz., 1. *The analytical process:* and, 2. *The calculation and arrangement of the results.*

1. The Analytical Process.

The performance of the analytical process is divided into two parts, viz., 1, operations and experiments at the spring or well; and, 2, operations and experiments in the laboratory.

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* Compare the chapter on the same subject in *Fresenius's* "Qualitative Analysis," 5th Edition, § 209.

† *Mazade, Henry* ("Journ. de Pharm. et de Chim.," 3 série, 24, 305; "Journ. f. prakt. Chem.," 62, 29).

‡ If they contain oxide of lead, oxide of copper, &c., which might proceed from metal tubes, stopcocks, &c., the real origin of the oxides must be most carefully ascertained (see "Qualitative Analysis").

A. OPERATIONS AND EXPERIMENTS AT THE SPRING OR WELL.

I. APPARATUS AND OTHER REQUISITES.

§ 207.

1. A pipette of 200 cubic centimetres capacity. Fig. 131 represents a pipette in a travelling case, as recommended by *Fr. Mohr.* A common siphon may also be used instead, with the lower orifice somewhat narrow. The capacity of this is ascertained by filling it with water, and measuring the contents in a graduated glass.

2. Four bottles with well-fitting corks; each of these bottles should hold about 300 c.c.

3. An accurately graduated thermometer, with plain scale.

4. A mixture of 2 volumes of solution of ammonia and 1 volume of solution of chloride of calcium or chloride of barium (§ 139, I., *b*, *a*). This mixture is boiled. It is filtered at the spring or well.

5. About 8 white glass bottles of 1½— 2 litres capacity, with well-fitting stoppers; ground-glass stoppers answer the purpose best. If corks are used, it is advisable to cover them with a thin piece of vulcanized india-rubber.

6. Some larger bottles, holding together at least 50 pounds of water, with well-fitting corks or glass-stoppers; instead of these a small carboy may be used.

7. A litre and a half-litre flask.

8. 1 middle-sized and 2 large funnels.

9. Swedish filtering paper.

10. Flasks, beakers, lamp, glass rods, glass tubes, caoutchouc tubes, files, scissors, knife, corks, string, &c.

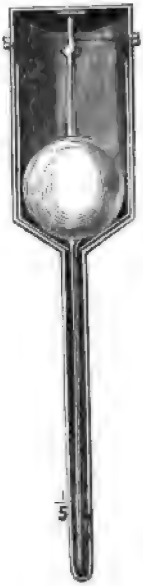

Fig. 131.

11. Reagents, more especially the following: ammonia, hydrochloric acid, acetic acid, nitrate of silver, chloride of barium, oxalate of ammonia, tannic acid and gallic acid (or infusion of galls), tincture of litmus (freshly prepared), test papers. Besides these articles, the following are also required under certain circumstances:—

a. If the Water contains Sulphuretted Hydrogen or an Alkaline Sulphide.

12. A solution of known strength of iodine in iodide of potassium. This must be very dilute; the best way is to prepare it by adding to 1 volume of *Bunsen's* solution of iodine (§ 146, 1) 4 volumes of water; which gives a mixture containing in 1 c.c. about 0·001 grm. of iodine.

13. Starch.

14. A burette with compression clamp, and several pipettes.

15. A solution of arsenious acid in hydrochloric acid, or of arsenite of soda; also the reagents and apparatus mentioned in § 208, 9.

b. If the Water contains a large proportion of Protoxide of Iron, which it is intended to estimate volumetrically at the Spring or Well.

16. A solution of permanganate of potassa. For waters abounding in iron, this solution must be of such a degree of dilution that 100 c.c. of it convert about 0·1 grm. of iron from the state of protoxide to that of

sesquioxide. If the water contains only a moderate proportion of iron, the solution must be still more largely diluted. As it is necessary to fix the strength of the solution on the spot, a burette, a pipette, and weighed pieces of pianoforte wire, or a standard solution of oxalic acid (§ 112, *b*, 2, *cc*), are also required.

c. If it is intended to determine the whole of the Gases dissolved in the Water.

17. A glass globe closed by a caoutchouc plate; also a long gutta-percha tube with brass stopcock or caoutchouc valve (for the latter, see § 185, *b*).

18. Another caoutchouc valve of greater width; the width of the caoutchouc tube must correspond to that of the neck of the globe (17).

19. An ebullition globe.

20. A graduated gas receiver, and

21. Several non-graduated gas-receivers, properly arranged for sealing.

22. A blow-pipe for sealing. To give the operator the free use of both hands, *Bunsen* recommends the arrangement shown in Fig. 132. (a) is a small lamp, holding about 3 grammes of oil; this is attached to the blow-pipe, by means of a somewhat flexible wire with ring (b), through which the nozzle of the blow-pipe passes. The proper position is given to the flame by bending the wire. The cork (c) serves as mouth-piece, to enable the operator to hold the apparatus between the teeth.

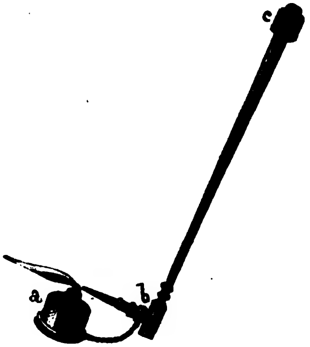

Fig. 132.

For a more detailed description of the other apparatus (17—21), see § 208.

d. If it is intended to determine the free Gases evolved at the Spring or Well.

23. A number of test-tubes, holding 40—60 c.c. each (see Fig. 133), (a) drawn out in the blow-pipe flame to the thickness of a small straw,

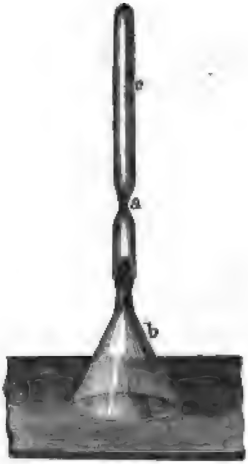

Fig. 133.

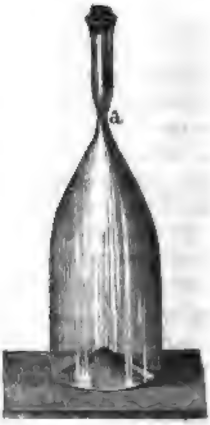

Fig. 134.

and connected air-tight with a funnel as shown in the drawing. They are intended to collect the gases at the spring, for subsequent examination in the laboratory. For the collection of large quantities of gas, bottles, with the neck drawn out (Fig. 134), are used instead of test-tubes.

24. A long glass tube of such small diameter, that it may be passed through the drawn-out narrowed parts of the tubes or bottles described in 23.

25. In cases where it is intended simply to estimate gases absorbable by solution of potassa (carbonic acid, sulphuretted hydrogen), without determining the other gases, which are not absorbed by that agent, only a graduated tube, some solution of potassa, and a small funnel are required.

If the water evolves sulphuretted hydrogen, the analyst must provide himself, in addition to the above enumerated articles, with,

26. A flask with the neck somewhat drawn out, and provided with a caoutchouc tube and compression clamp; and,

27. An ammoniacal solution of chloride of copper (see § 208, 14).

II. ANALYTICAL PROCESSES.

§ 208.

1. Examine the appearance (color, clearness, &c.) of the water. A water will often look clear at a first glance, and yet upon closer inspection in a large white bottle show a few or even a great many colored or colorless flakes, &c. In such cases, the bottle is allowed to stand a day or two, and the clear water then decanted; the matters which may have subsided are afterwards examined under the microscope. This examination often reveals the presence of infusoria, plants of the lowest order, &c.*

2. Observe whether there is disengagement of gas; whether the water in a glass forms small pearly bubbles; and whether it evolves gas when shaken in a half-filled bottle.

3. Examine the taste and smell of the water. To detect very minute portions of odorous matters, half fill a tumbler or, better still, a water bottle, cover with the hand, shake vigorously, take off the hand, and smell the water.

4. Ascertain the *reaction* of the water, by testing with the several test papers (or, better still, with blue and but very slightly reddened tincture of litmus); and observe whether the color which the paper has acquired, changes upon drying in the air.

5. Examine the *temperature* of the water. The simplest and best way of effecting this is, if practicable, to plunge the thermometer into the spring, and to note accurately the height of the mercury whilst the thermometer is still in the water; or a large bottle with a thermometer in it is filled with water by immersion in the spring, and left some time in the latter; it is then taken out, and the height of the thermometer in the flask accurately noted. If the water flows from a pipe, it is received in a large narrow-necked glass funnel which will allow about as much water to run out as enters. The thermometer is fixed in the middle of the contents of the funnel, and the height of the mercury marked after some time.

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* Compare *Schulz* ("Jahrbücher des Vereins für Naturkunde im Herzogthume Nassau," Heft VIII., p. 49).

In addition to the temperature of the spring must be noted also :—

a. The date.

b. The temperature of the air.

c. The circumstance whether the temperature of the water is constant or varies in the different seasons of the year; which may generally be ascertained on the spot.

6. Fill the bottles specified in § 207, 5, with water. This must be effected with great care, to prevent turbid water entering into the bottles, which is very likely to happen if the bottle accidentally grazes the bottom or sides of the well. If you cannot succeed in procuring the water quite clear, filter it in 4 of the 8 bottles, using for this purpose large funnels with plaited filters of Swedish paper, which will greatly expedite the process of filtration. Close the bottles securely, and mark them.

As impurities occasionally float on the surface of the water, it is always advisable to submerge the bottles entirely, and to a sufficient depth. In cases where it is desirable to avoid the least agitation of the water in the well, the bottle or flask should be provided with the apparatus illustrated in Fig. 135.

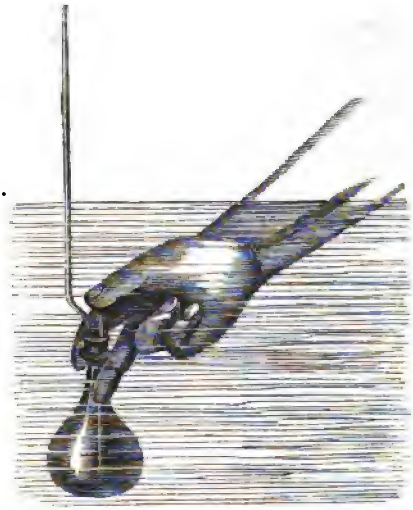

Fig. 135.

As soon as the thumb is removed from the mouth of the short tube, the water rushes into the vessel, whilst the air escapes through the other tube, which opens above the surface of the water. If the water lies beyond the reach of the length of the operator's arm, the bottle or flask is tied to a rod, or let down into the well suspended by a string, and with a weight attached. To keep the bottle or flask in the upright position, a net may be used, with a sufficiently large hole in the middle, through which the neck of the bottle is thrust, the net being then gathered and tied under the bottom of the bottle, and a sufficiently heavy weight attached to it. The bottle so prepared is then let down into the water by a string tied round the neck.

7. Pour about 50—100 c.c. of the freshly filtered and perfectly clear ammoniacal solution of chloride of calcium or chloride of barium (§ 207, 4) into each of the 4 bottles specified in § 207, 2.

8. Transfer to each of the 4 bottles a definite quantity of the water in the manner directed § 139, I., *b*; insert the corks tightly, and secure them with a string.

9. If the water contains hydrosulphuric acid, determine this by the standard solution of iodine (§ 207, 12), exactly in the manner directed § 148, 1, *a*. If the water contains an alkaline carbonate, in presence of a tolerably large proportion of free carbonic acid, this necessitates no

modification of the process, and there is no need of adding acetic acid or chloride of barium, since bicarbonate of soda is without action upon iodine solution.

In the analysis of alkaline mineral waters, the question arises, how much of the sulphur compound found should be calculated as sulphuretted hydrogen, and how much as sulphide or hydrosulphuretted sulphide? As it is, therefore, of importance to know whether the water will, upon long-continued transmission of an indifferent gas, wholly or partially loose the sulphur compound which it contains, a portion of the mineral water is weighed off, in a flask closed by a cork with two perforations, into one of which is fitted a tube reaching to the bottom of the flask, into the other, a tube bent at a right angle, which does not project beyond the cork; through the former hydrogen gas, which has been passed, first through solution of chloride of mercury, then through solution of potassa, is conducted into the water; through the latter the evolved gas makes its exit from the flask. As soon as the issuing gas no longer decolorizes a small quantity of highly dilute solution of iodide of starch, which is a proof that it no longer contains sulphuretted hydrogen, the transmission of the hydrogen gas is discontinued, and the sulphur remaining in the water in the flask determined by iodine solution, or as tersulphide of arsenic. The operation generally takes several hours; it should be conducted in a cool and shady place.

The sulphur compound remaining in solution in the water in the flask is, in the case of mineral waters containing also free sulphuretted hydrogen, hydrosulphuretted sulphide.

Although this method, recommended also by *W. B.* and *E. Rogers* ("Journ. f. prakt. Chem.," 64, 123), is well adapted for waters containing only, or almost exclusively, free sulphuretted hydrogen, and no hyposulphite,* it cannot be used for sulphur waters containing chiefly soluble sulphides, or hydrosulphuretted sulphides, and besides these—as is often the case—hyposulphites.

In waters of this description, the sulphur in combination with hydrogen or metal is determined jointly, in the first place. This is effected best by means of a solution of cadmium, which is as sensitive as any other metallic salt (Analyt. Notes and Experiments, No. 94), and is not affected by hyposulphite of soda. However, the precipitated sulphide of cadmium being liable to contain chloride of cadmium, cannot be weighed direct (Analyt. Notes and Experiments, No. 95), but the sulphur must be determined in it as stated § 148, II., 2.

A fresh portion of the water is now taken, and first the free sulphuretted hydrogen expelled from it, then the sulphuretted hydrogen present as sulphur acid, in combination with metallic sulphide; the evolved gases are determined by transmitting them through an ammoniacal solution of nitrate of silver. The sulphur combined with metal to simple sulphide is then estimated by the difference (unless a bisulphide be present).

To effect this object, the same method may be employed which *Simmler* used in his excellent analysis of the mineral water of *Stachelberg*. The free sulphuretted hydrogen gas is first expelled from the water by means of pure hydrogen gas, with the aid of an exhausting syringe; solution of sulphate of protoxide of manganese is then added, through a funnel tube, to the water from which the free gas has been removed; the sulphuretted hydrogen which is present as sulphur acid in combination with metallic sulphide, is thus also expelled.

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* Compare *Fresenius'* Analysis of the Mineral Water of *Weilbach*, "Journ. f. prakt. Chem.," 70, 8.

The fluid is filtered off from the sulphide of manganese, and the warm filtrate mixed with solution of neutral nitrate of silver; if a hyposulphite is present, a precipitate of sulphide of silver will fall down, which generally contains also chloride of silver. This precipitate is filtered off, the chloride of silver removed by ammonia, the washed sulphide of silver dissolved in nitric acid, the silver in the solution determined as chloride of silver, and the hyposulphurous acid calculated from the results. Compare § 168 (**211**). I think I need hardly observe that the silver in the sulphide need not be determined at the well.

The filtered precipitate of sulphide of manganese contains the sulphur present in the analysed water in form of simple metallic sulphide; but if the water contains a bisulphide* the protosulphide of manganese is mixed with the sulphur which was combined with the monosulphide to bisulphide; the free sulphur thus mixed with the sulphide of manganese is left undissolved upon treating the precipitate with hydrochloric acid.

For the details of the operation and the apparatus employed for the expulsion of the sulphuretted hydrogen, I refer to *Simmler's* paper on the subject, in the "Journ. f. prakt. Chem.," 71, 27.

10. If the water contains a somewhat large quantity of carbonate of protoxide of iron,—which is indicated by the rather dark violet color exhibited upon addition of gallic and tannic acids—endeavor to determine the carbonate of protoxide of iron volumetrically with the aid of the dilute solution of permanganate of potassa (§ 207, 16). Compare § 112, *b*, 2, *β*). Take about 500 c.c. of the water, and perform the experiment in a white bottle, standing on a sheet of white paper; mix the water previously with dilute sulphuric acid.

Repeat the experiment several times until you obtain sufficiently constant results.†

If the water smells of sulphuretted hydrogen, or if it contains a notable proportion of organic substances, this method cannot be employed.‡

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* If the water contains a bisulphide, it will in a large quantity appear yellowish.

† By this expeditious process we may readily ascertain how much protoxide of iron the water of a chalybeate spring loses in its passage to the reservoir, and thence to the baths; or after being kept for a shorter or longer time in a stone jar. The quantitative estimations of the iron, which I made by this process in a preliminary examination of the springs of Schwallbach, corresponded almost exactly with the results of a careful gravimetric analysis made afterwards in the laboratory. The same process is also of essential service in collecting the water of chalybeate springs, as it enables the operator at once to examine on the spot every small contributory.

‡ The following modification which, however, I have not yet tried, might be adopted in the analysis of mineral waters in which hydrosulphuric acid only is present with the protoxide of iron. Determine the amount of solution of iodine which corresponds to a certain definite quantity of solution of permanganate of potassa, in its action upon an equal quantity of very dilute pure sulphuretted hydrogen water. Test 500 c.c. of the mineral water with solution of iodine, and another 500 c.c. with solution of permanganate of potassa: the former process gives the amount of the sulphuretted hydrogen present in the analysed water; the latter, after deducting from the quantity of solution of permanganate of potassa used, an amount exactly corresponding in its action upon sulphuretted hydrogen to the quantity of solution of iodine used, gives the proportion of the iron contained in the analysed water.

11. To determine the whole of the gases which the water holds in solution, fill the globe specified in § 207, 17, and illustrated in Fig. 136, to the brim with the mineral water, by filling it first with the mineral water, then letting it down into the well, either tied to a rod, or with weights attached to it, and sucking out the contents through the gutta-percha tube (a), which reaches down to the bottom of the globe, until the water originally present in the vessel is entirely replaced by fresh water from the spring. The cock (b) serves to prevent the water in the tube receding during the necessary intervals of cessation from sucking; or a small piece of vulcanized India-rubber tubing may be substituted instead, which is closed by pressing between the fingers. The globe is closed by a plate of vulcanized India-rubber (c), which, by its elasticity, permits the lateral insertion of the tube (a) through a slit, whilst completely closing the mouth of the globe after the withdrawal of the tube. When the water in the globe has been entirely replaced by fresh mineral water from the spring, withdraw the sucking tube (a), and take the globe out of the well. Then connect it promptly with a caoutchouc valve (see Fig. 137 (a), compare § 185, *b*), which is filled with boiled water, and tied (*R. Bunsen*, "Gasometrische Methoden," translated by Roscoe).

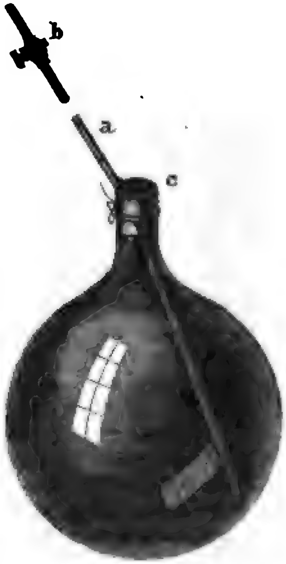

Fig. 136.

If the water flows from a pipe, connect this with a caoutchouc tube, introduce the latter into the globe, down to the bottom; let water run in for some time after the globe is full, and close finally with the caoutchouc valve as just now directed.

Then connect the other end of the valve (a) with the tube (b), and the latter again, after pouring some water into it, with the graduated tube (c), by means of another caoutchouc valve (d). The capacity of the graduated tube (c) must be at least as 3 to 2 to the volume of the gas which the water holds in solution, measure in the cold, and at the common pressure.

Now incline the apparatus a little, sufficient to bring some of the water in the tube (b) into the body of the bulb, and boil, with the valve (a) closed, and the valve (d) open, until the atmospheric air is completely expelled, and replaced by aqueous vapor; then close the vulcanized india-rubber tube (e) by a ligature or a compression clamp. When the apparatus is cold, open the valve (a), and apply heat; the water in the globe begins immediately to boil, and the gas which it holds in solution escapes into the *vacuum*. Continue the application of heat for about $1\frac{1}{2}$ hour, without exceeding 194° F., which will keep the water in the globe in constant ebullition, and completely expel the gases from it. After this, heat a little more strongly, until, owing to the greater expansion of the vapors, the boiled water exactly reaches the caoutchouc valve (d). The instant this is the case, tie the ligature round (d), disconnect the tube (c) from (b), open (c) under mercury, by taking the ligature off (e), and note the volume of the gas in (c), with due regard to the state of the barometer and thermometer, and to the height of the mercury in the tube (*R. Bunsen,* "Gasometrische Methoden," page 18). If there is no graduated tube at hand, a non-graduated one of known capacity may be used instead; in which case, as soon as, after taking off the ligature, the level of the mercury is inside and outside the same, the ligature is again drawn tight, and the mercury which has entered the tube transferred to a graduated cylinder, where it is measured. The volume found is subtracted from the known capacity of the tube: the difference expresses the volume of gas expelled from the water.

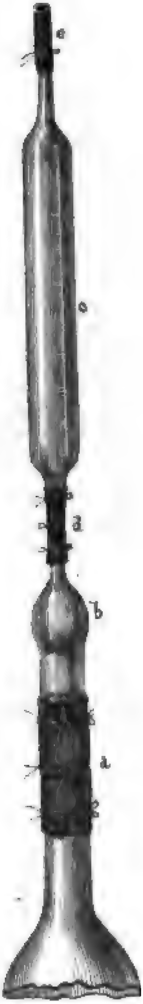

Fig. 137.

As it is not likely the operator will take with him to the well the entire apparatus required for the actual analysis of the expelled gases, the latter must be taken to the laboratory, in sealed tubes. For this purpose non-graduated tubes of a similar form to (c) are substituted for the latter; these tubes are drawn out at both ends, near the thicker part, so as to readily admit of sealing. The expulsion of the gases from the water is effected as just now described, and, when the operation is over, and the ligature tied round (d), the two drawn-out ends of the tube are sealed in the blowpipe flame, the apparatus described § 207, 22, being employed for the purpose. It is advisable to fill 2 or 3 tubes in this manner. As the total quantity of the gas in a given definite amount of the water is known by the first experiment, it is a matter of indifference whether the tubes used for carrying the gas to the laboratory, contain the whole of the gas expelled from the water, or whether a small quantity of it is left in the globe.

12. If it is wished to *accurately* ascertain the nature of the free gases spontaneously disengaged from the water of the well, they should be received in tubes of the form described in § 207, 23, and illustrated in Fig. 133, or in bottles with drawn-out neck, as shown in Fig. 134. After filling the tubes or bottles with the mineral water, and connecting them air-tight with the funnel, by means of a cork or an india-rubber tube, the apparatus, with the mouth of the funnel turned upward, is completely submerged under the surface of the well, and water sucked out through a narrow tube, reaching down to the bottom of the tube or bottle, until the water of the first filling is entirely replaced by a fresh quantity, which has not been in contact with air. The apparatus is now inverted, under the water, which causes the spontaneously disengaged gas to ascend through the funnel. Should the gaseous bubbles be detained in the neck of the funnel, or in the narrow part of the tube or bottle, they may readily be dislodged by tapping the rim of the funnel against a solid, hard body. A sufficient quantity of gas is allowed to enter to fill the tube or bottle and the neck of the funnel; a dish is now placed beneath the

funnel, on which the latter is supported, and the apparatus then lifted out of the water; the drawn-out narrowed part of the tube or bottle is gently heated in the blowpipe flame (see § 207, 22), and then sealed. As the column of water in the funnel above the level of the dish diminishes the pressure of the gas against that of the atmosphere, expansion of the glass need not be apprehended (*R. Bunsen*, "Gasometry," by Roscoe). It is advisable to fill several tubes or bottles in this manner.

13. As the evolved gases generally consist only of carbonic acid, oxygen, and nitrogen, it often suffices to determine the first in the direct way, and to estimate the sum of the other two from the loss. For this purpose, receive the gases in a somewhat narrow graduated cylinder; when the latter is quite full, close the mouth with the finger, invert in a glass containing solution of potassa, and determine the quantity of the unabsorbed gas. Repeat the experiment several times.

14. If sulphuretted hydrogen is given off, fill a rather large-sized flask, with the neck somewhat drawn out (§ 207, 26), with the mineral water, push over the neck a piece of wide caoutchouc tubing provided with a strong compression clamp, insert into the other end of the caoutchouc tube a funnel, and fill the latter also with water. Invert the whole under the surface of the water, and receive the gases. When the flask is full, close the compression clamp, and invert the flask in a beaker containing solution of chloride of copper mixed with ammonia in excess; open the compression clamp, and let a sufficient quantity of the solution enter the flask; close the clamp, shake, allow the mixture to stand some time, filter off the sulphide of copper formed, and determine the sulphur in it as directed § 248, II., 2, *a*. Calculate from the quantity of sulphur the volume of sulphuretted hydrogen. By subtracting this from the gases absorbable by solution of potassa and determined in 13, you obtain the volume of the carbonic acid.

15. Fill the large bottles (§ 207, 6) with the mineral water. It is generally unnecessary to filter it.

16. Pay attention to every particular connected with the spring or well, and to every circumstance which may have a bearing upon the investigation: as, for instance, and more particularly, how much water and how much free gas the spring yields;—whether the quantities of water and of free gas remain the same or not at different periods of the year, and with the changes in the height of the water in neighbouring rivers;—whether the level remains the same or not;—whether a muddy deposit or solid sinter forms in the outlet pipes or in the reservoir (in which case a tolerably large quantity of the deposit must be taken to the laboratory for examination);—to what geological formation the mountain belongs from which the water is derived;—the depth at which the spring rises;—the nature of the basin;—the predominant action and effects of the water, &c.

B. OPERATIONS IN THE LABORATORY.

I. QUALITATIVE ANALYSIS.

This is effected in the manner described in my "Qualitative Analysis,"* 5th Edition, § 209.

II. QUANTITATIVE ANALYSIS.

§ 209.

The course to be pursued in the quantitative analysis of mineral waters differs according to the presence or absence of alkaline carbonates. As the analytical course is more simple in the case of alkaline than in that of non-alkaline waters, we will begin here with the latter, which, in fact, almost entirely includes the processes, &c., required in the analysis of alkaline waters; and we will afterwards point out the modifications required, respectively, in the analysis of alkaline, and of sulphuretted waters. We proceed upon the assumption that all the matters are present which are usually found associated in saline springs.

As the evaporation of large quantities of water, which is necessary to effect the determination of the substances present in very minute proportions, consumes much time, it is advisable to begin with this operation and to carry it on concurrently with the other analytical processes.

From 10,000 to 20,000 grammes of the water are gradually evaporated in a platinum or porcelain dish,† with addition of a sufficient quantity of absolutely pure carbonate of soda‡ to impart a feebly alkaline reaction § to the fluid. The best way is to conduct the evaporation in a separate room, to which no one but the analyst has access, over gas or spirit-lamps, or on the sand-bath; that the greatest cleanliness is necessary in the operation, need hardly be mentioned; it is not advisable, therefore, to allow this operation to be performed by another person. When the fluid is somewhat concentrated, the evaporation is continued on the water-bath, or on a very moderately heated sand-bath, until the residue is perfectly dry.

The actual analysis of the water is preceded by the

DETERMINATION OF THE SPECIFIC GRAVITY.

Equalize the temperatures of a bottle of the mineral water and a bottle of distilled water, and note the height of the thermometer. Fill an accurately tared small bottle of at least 100 grammes capacity, provided with a well-fitting glass stopper,|| with the distilled water, and weigh;

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* Mineral waters which have been kept a long time in stone bottles, often smell of sulphuretted hydrogen, though in the fresh state they were entirely free from that odor. This is owing to the circumstance that the contact with the moist cork, or some other organic substance, reduces a portion of the sulphates to sulphides, from which the free carbonic acid afterwards evolves sulphuretted hydrogen.

† If you use a porcelain dish, you must renounce the detection and determination of alumina.

‡ Free more especially from phosphoric acid, alumina, and manganese.

§ The addition of carbonate of soda is intended to prevent volatilization of hydrobromic or hydriodic acid from bromide or iodide of magnesium. If a mineral water contains no sulphuric acid, a very small quantity of sulphate of soda is also added, to supply sulphuric acid for the subsequent separation, as sulphates, of the baryta or strontia which may be present (see § 209, 7, *b*).

|| A flask with a long perforated ground stopper, as illustrated in Fig. 138 (a *Pyknometer*), answers the purpose best.

empty the bottle, refill it with the mineral water, and weigh again. The quotient obtained by dividing the weight of the mineral water by that of the distilled water, gives the specific gravity of the former. Take care that there are no gas bubbles in the bottles filled with water.

The respective quantities required for the estimation of the several constituents may be determined either by weight or by measure. If they are estimated by measure, the small bottle or flask may be used which has served for the determination of the specific gravity; or any other measuring vessel may be employed. I prefer determining them by weight, as this best enables the operator to take given quantities in round numbers in grammes.

1. Estimation of the Total Amount of the Fixed Ingredients.

Weigh 200—1000* grammes of the mineral water in a small flask, and evaporate cautiously and gradually, in a weighed platinum dish, at a temperature below the boiling point, adding from time to time fresh quantities of water. If the water abounds in gas, cover the dish, at first and after every fresh addition of water, with a large watch-glass. The evaporation may be conducted over the lamp. Terminate it on the water-bath, and dry the residue in the air- or oil-bath, at a temperature of 356° F., until repeated weighings give the same result; then note the weight.† Fill the dish again one-half with distilled water, and add from time to time a drop of dilute sulphuric acid, until you are quite sure that the quantity of the acid added is sufficient to convert all the salts into sulphates; keep the dish covered during this operation with a large watch-glass; evaporate now to dryness, ignite the residue (§ 97, 1), and weigh. The weight found supplies a good control of the analysis (see below). Residues abounding in carbonate of lime should be treated first with hydrochloric acid, until it no longer produces effervescence, and then evaporated with sulphuric acid.

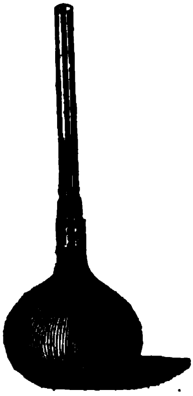

Fig. 138.

2. Determination of the Sulphuric Acid.

If chloride of barium produces at once a marked turbidity in the water acidified with hydrochloric acid, take about 500 grammes of the water, mix with hydrochloric acid, add chloride of barium, allow the mixture to subside for 24 hours, and then determine the sulphate of baryta, as directed § 132, I., 1. If the turbidity produced by the chloride of barium is only slight, evaporate 1000—2000 grammes of the water, with addition of hydrochloric acid, to $\frac{1}{3}$, $\frac{1}{4}$, or less, and treat the residual fluid as just now directed.

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* According to the degree of concentration of the water.

† The quantity of the chloride of magnesium suffers in this operation a slight diminution of weight, as a small portion of it decomposes with the water into hydrochloric acid, which escapes, and magnesia, which remains. However, the error arising from this is but trifling, and may mostly be disregarded, since, for the reasons given in § 205, I., 7, the total amount of the fixed ingredients estimated collectively, can never be expected to correspond exactly to the sum total of the several constituents separately determined. Still this defect may be corrected by evaporating the water with a weighed quantity of ignited carbonate of soda (*Mohr*), or with a known quantity of sulphate of potassa (*Tillmann*, "Annal. d. Chem. u. Pharm.," 81, 369). In the latter case, the elements of $Mg\,Cl$ transpose with those of $2\,(K\,O,\,S\,O_3)$, forming $K\,Cl$ and a double sulphate of potassa and magnesia $(K\,O,\,S\,O_3 + MgO,\,S\,O_3)$.

3. JOINT ESTIMATION OF THE CHLORINE, IODINE, AND BROMINE.

Acidify 50—1000 grammes of the water with nitric acid, precipitate with nitrate of silver, and determine the precipitate as directed § 141, I., *a*. Waters containing only a small proportion of chlorine must be concentrated before the addition of nitric acid. If this gives rise to the formation of a precipitate, the latter may be filtered off, or dissolved by nitric acid, before precipitating with solution of nitrate of silver.

4. ESTIMATION OF THE TOTAL AMOUNT OF THE LIME, MAGNESIA, IRON, MANGANESE (if that metal is present in somewhat large proportion), SILICIC ACID, AND THE ALKALIES.

Weigh one of the bottles filled at the well with perfectly clear or, if necessary, filtered water (§ 208, 6), with its contents; pour some of the water cautiously, and without spilling a drop, into a beaker, and add to the water, both in the bottle and beaker, hydrochloric acid until the latter slightly predominates. Cover the bottle with a watch-glass, the beaker with a glass plate, and apply a very gentle heat, until the carbonic acid has escaped. Then evaporate the contents of both vessels, in a platinum or porcelain dish, to dryness, and separate the silicic acid as directed § 140, II., *a*. Mix the hydrochloric acid solution with chloride of ammonium, add an excess of ammonia free from carbonic acid, then some yellowish sulphide of ammonium; close the vessel, which is now nearly full, and let the mixture stand 12 hours at a gentle heat; then filter quickly, and wash the precipitate with water to which some sulphide of ammonium has been added.

a. The *precipitate* may be assumed to contain iron, manganese, alumina, phosphoric acid, and possibly also traces of lime and magnesia. In most cases only the sesquioxide of iron in it is determined, sometimes also the protoxide of manganese; whilst the traces of phosphoric acid and alumina are determined in the residue left upon the evaporation of the large bulk of 10,000 or 20,000 grammes of the water (see beginning of § 209).

Dissolve the precipitate by heating with hydrochloric acid; boil with some nitric acid and filter; nearly saturate with carbonate of soda, then add acetate of soda, boil and proceed generally as directed § 159 (57, *d*), to effect the separation of the sesquioxide of iron, together with the phosphoric acid and alumina* which may be present. Dissolve the precipitate in hydrochloric acid, precipitate the solution with ammonia, weigh the ignited sesquioxide of iron, and, by way of control, redissolve it, and determine the iron in the solution volumetrically (§ 113, 2).

Should there be a difference between the results of the two determinations, this must not be calculated as alumina or phosphoric acid; only imponderable traces of these two bodies would generally be likely to be present in the relatively small quantity of water operated upon.

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* Even though the water should contain little or no alumina, yet the precipitate may contain some, proceeding from the vessels used in the operations.

Care must be taken to see whether, upon dissolving the weighed sesquioxide of iron in hydrochloric acid, no more silicic acid is left than corresponds to the filter ash.

From the fluid filtered off from the basic acetate of the sesquioxide of iron, precipitate the manganese by chlorine, § 159 (**58**, β), or by sulphide of ammonium, § 159 (**54**). Test the filtrate for lime, and after this for magnesia. If traces of these substances are found, collect them on small filters, and ignite these jointly with the filters containing the principal bulk of the same substances (see *b*). Instead of precipitating the manganese with chlorine or sulphide of ammonium, you may also add a little chloride of zinc to the fluid, then precipitate with carbonate of soda, and determine the manganese in the ignited residue as directed in § 159 (**59**). Precipitate now the solution remaining in the flask with ammonia and sulphide of ammonium, and determine in the filtrate the traces of lime and magnesia which may be present.

Instead of employing this process, the iron and manganese can be determined directly by the volumetrical method; first the manganese as directed § 160 (**92**), then the iron in the residue.

b. From the *filtrate*, precipitate the lime with oxalate of ammonia, determine the lime by adding a sufficient quantity of pure oxalate of ammonia —quite free from potassa and soda—(§ 154, **30**). The weighed precipitate must be carefully tested for magnesia; if any of that earth is found, this must be determined separately, and subtracted, as pure magnesia, from the weight of the carbonate of lime containing magnesia.

Evaporate the fluid filtered off from the oxalate of lime in a porcelain dish to dryness, and heat the residue gently in a platinum dish (§ 42), to remove the ammonia salts. In the residue, separate the magnesia finally from the alkalies as directed § 153 (**18**). Dissolve the separated magnesia in hydrochloric acid, add ammonia, and precipitate as phosphate of ammonia and magnesia. By this course of proceeding, you avoid those mistakes which are so apt to arise from the presence of silicic acid and alumina, proceeding from the vessels used in the process. The chlorides of the alkali metals must, after weighing, be examined as to their purity (see § 152, 1, *a*, foot-note).

If the quantity of the sulphuric acid was small, the solution of the alkaline chlorides is free from that acid, since the trifling amount of sulphate has been decomposed by the ignition with chloride of ammonium. But as this can never be positively known, and as repeated evaporation with chloride of ammonium is somewhat tedious, the following proceeding may be adopted: transfer a few drops of the solution of the weighed pure chlorides of the alkali metals, by means of a glass rod, to a test tube, and add a few drops of alcoholic solution of chloride of strontium and a little spirit of wine. If no precipitate forms, this is a proof that the fluid contains no sulphuric acid, in which case add the contents of the test tube again to the solution, and determine the potassa in the latter as directed § 152 (**2**). But if a precipitate forms, treat the whole solution cautiously in the same way as the sample in the test tube; let the mixture stand some time, and then filter the fluid off from the precipitated sulphate of strontia, which determine as directed § 102. Estimate the potassa in the filtrate as directed § 152 (**2**). It is necessary to weigh the sulphate of strontia, that the quantity of the soda may be accurately calculated. The quantity of the soda is ascertained by subtracting from the weighed residue in the dish, 1, the chloride of potassium, and, 2, the weight of sulphate of soda corresponding to the sulphuric acid found. The remainder is chloride of sodium. The soda is then calculated from the sulphate of soda and chloride of sodium.

The foregoing method may in many cases, more particularly in presence of traces of manganese, be simplified, by mixing the fluid filtered off from the silicic acid at once with ammonia free from carbonic acid, filtering the precipitate, washing, redissolving in hydrochloric acid, and precipitating the solution again with ammonia. The precipitate so obtained is dried, ignited, weighed, redissolved in hydrochloric acid, the silicic acid, which may be left, determined, and the iron in the solution finally estimated volumetrically, by way of control. In presence of alumina and phosphoric acid the results of the volumetric determination are taken to be the more accurate. If you wish to ensure the precipitation of the manganese along with the iron, add to the solution hypochlorous acid, or chlorine water, before proceeding to precipitate.

It is often also preferred to determine only the lime and magnesia (as directed § 154, 30) in the fluid filtered off from the sesquioxide of iron, and to estimate the alkalies in a separate portion of the water. For this purpose, about 500—1000 grammes of the water are boiled with pure milk of lime, best in a silver dish, then filtered, the filtrate concentrated, the lime precipitated by carbonate and a little oxalate of ammonia, filtered off, and the alkalies in the filtrate determined as chlorides. If the water contains only a small proportion of sulphuric acid, it suffices in evaporating the fluid containing the alkalies, to add, towards the end of the process, some chloride of ammonium; but, if the proportion of sulphuric acid present is large, it is necessary to add at once, before the addition of the milk of lime, a quantity of chloride of barium equivalent to the known amount of the sulphuric acid. In this process also, proper attention must be paid, as regards the chlorides of the alkali metals, to the remarks in the foot-note to § 152, 1, *a*.

5. Estimation of the Lime, Magnesia, Iron (and Manganese), in the Precipitate formed on boiling the Water; and of the Lime and Magnesia in the boiled Water.

Boil 500—1000 grammes of the water in a glass flask for about 2 hours, replacing the evaporated water from time to time by distilled water. (If this precaution were neglected, sulphate of lime might separate in conjunction with the carbonates of the alkaline earths.)

Filter the precipitate and wash.

Separate and determine the lime and magnesia in the filtrate as directed § 154 (30).

Dissolve the precipitate in dilute hydrochloric acid, heat with some nitric acid, and determine the iron (manganese), lime, and magnesia in the solution as in 4.

This course of proceeding will enable the operator to judge how much of the lime and magnesia is present as bicarbonate. However, it must not be lost sight of, that the simple carbonates of lime and magnesia are not altogether insoluble in water, and, to be as nearly accurate as possible, proper correction must accordingly be made for this in the calculation.

6. Estimation of the total Amount of Carbonic Acid present.

The bottles filled at the spring, as stated § 208, 8, are employed for the purpose. The determination is effected, in 2 or 3 bottles, exactly as directed § 139, I., *b*. The results must pretty nearly agree; the mean of them is taken. If the water which has given the baryta or lime precipitates, has been measured, the number of cubic centimetres must be multiplied by the specific gravity found, to ascertain the number of grammes of water to which the carbonic acid corresponds.

7. ESTIMATION OF THE BARYTA, STRONTIA, LITHIA, PROTOXIDE OF MANGANESE, ALUMINA, AND PHOSPHORIC ACID; AND ALSO OF THE IODINE AND BROMINE.

The residue left upon evaporating 10,000—20,000 grammes of the water (see the beginning of this paragraph), is used to effect the determination of these substances, which are present only in small proportions.

Triturate and heat the perfectly dry saline mass repeatedly with spirit of wine of 96 per cent., until you are quite sure that the iodides and bromides of the alkali metals which may be present are completely dissolved.

a. Add to the *alcoholic filtrate* 2 drops of pure solution of potassa, and distil, in a flask, on the water-bath, to dryness, boil the residue repeatedly with absolute alcohol, distil the filtrate, after addition of a drop of pure potassa solution, again to dryness, and ignite the residue very gently, to destroy the organic matter which may be present.

The trifling residual saline mass is treated best as directed § 169 (**227**), more especially when there is some uncertainty as to the presence of iodine; since this course of proceeding leads not only to the detection of the latter substance, but also to its determination and separation, so that the bromine may also afterwards be determined. For the details of the process, I refer to § 169, 3 (**226**—**229**), where the subject has been fully treated.

As traces of lithia may have passed into the alcoholic solution, remove, after the precipitation of the bromine, the excess of silver from the filtrate, by means of hydrochloric acid, and add this solution as well as the residual saline mass left upon boiling the residue of the first distillation with absolute alcohol, which consists chiefly of chloride of sodium, to the principal residue of the mineral water.

b. Treat the total residue left, upon boiling with alcohol, with water, add hydrochloric acid, cautiously, until the solution is acid, and then evaporate to dryness. Dissolve the saline mass in water, with addition of very little hydrochloric acid, add an equal volume of alcohol,* allow the mixture to stand for 24 hours, and then filter off the fluid from the undissolved residue, which, besides silicic acid, must contain all the baryta and strontia present, in the form of sulphates, and generally contains also sulphate of lime.

aa. Wash and dry this *residue*, and, after adding the filter ash, boil with carbonate of soda and solution of soda, to dissolve the principal portion of the silicic acid. Fuse the undissolved part with some carbonate of soda and potassa, and treat the fused mass with boiling water, until no trace of sulphuric acid can be detected in the washings. Dissolve the residue—which must contain baryta and strontia in the form of carbonates—in a very small proportion of dilute hydrochloric acid, and separate the baryta, strontia, and lime, as directed § 154 (**26**).

bb. Oxidize the *fluid* filtered from the silicious residue, after evaporating the alcohol, with nitric acid, *nearly* neutralize it with *absolutely* pure carbonate of soda or potassa (quite free from phosphoric acid), and then precipitate with perfectly pure carbonate of baryta (free from lime, strontia, and phosphoric acid). Let the mixture stand in a stoppered flask for 12 hours in the cold, then filter, and wash the precipitate thoroughly.

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* Sulphate of strontia is slightly soluble in *aqueous* solution of chloride of sodium.

a. Heat the precipitate—which, besides the excess of carbonate of baryta and sulphate of baryta, contains all the sesquioxide of iron, and also alumina* and phosphoric acid, and may contain, besides, traces of fluoride of calcium—with hydrochloric acid, and throw down the baryta from the solution by sulphuric acid added very slightly in excess. Evaporate in the water-bath, to remove the excess of hydrochloric acid as far as practicable; dissolve the residue in water, transfer the solution to a small flask, add tartaric acid, then ammonia, and allow the fluid to stand 12 hours. If a trifling precipitate subsides, filter and examine this; it may contain fluorine† and phosphoric acid in combination with lime. Mix the clear or filtered fluid with sulphide of ammonium, and let the mixture stand in a stoppered flask until the fluid exhibits a pure yellow color. Filter from the sulphide of iron, and evaporate the filtrate in a platinum dish, adding some pure carbonate of soda—that there may be an excess of fixed base for the phosphoric acid—and some pure nitrate of potassa, the more readily to destroy the tartaric acid. Finally heat to redness until the residue looks perfectly white. Then add water and hydrochloric acid until complete solution is effected,‡ and precipitate the clear fluid with ammonia. If a precipitate forms (hydrate of alumina, or phosphate of alumina, or a mixture of both), filter and weigh. Mix the filtrate with a little sulphate of magnesia. If this gives a precipitate of *phosphate* of magnesia and ammonia (which determine as directed § 134, I., *b*), the alumina precipitate may be entered in the calculation as *phosphate of alumina* (Al_2O_3, PO_5). But if no precipitate forms, the phosphoric acid in the alumina precipitate has to be determined as directed § 134, I., *b*, *β*. I have to remark here, once more, that the alumina found can only be calculated as an ingredient of the analysed water, if the processes of evaporation, &c., have been conducted in platinum or silver vessels.

β. Mix the fluid filtered from the precipitate produced by carbonate of baryta, in a stoppered bottle, with chloride of ammonium, ammonia, and sulphide of ammonium. Let the mixture stand 12 hours, and then filter the precipitated sulphide of manganese; dissolve it in hydrochloric acid, heat, throw down by a little sulphuric acid the trace of baryta which is generally still present, then add, without filtering off the precipitate, ammonia and sulphide of ammonium, let the mixture stand 12 hours, filter, wash, treat the precipitate with hydrochloric acid, filter again, and determine finally the manganese as directed § 109, 1, *a*. Or, mix the hydrochloric acid solution of the first precipitate of sulphide of manganese with some chloride of barium, precipitate with carbonate of soda, and determine the manganese by the volumetrical method as directed § 159 (59).

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* If the evaporation of the 10,000 or 20,000 grammes of the water has been conducted in a porcelain dish, the residue left upon that evaporation (and accordingly also the fluid of *bb*, and the precipitate thrown down from it) contains, besides the alumina originally present in the water, also alumina derived from the porcelain evaporating dish.

† As the greater portion of the fluorine has, in the evaporation with hydrochloric acid, volatilized as fluoride of silicon, the fluorine found in *a* gives, of course, no clue to the proportion of that element contained in the water.

‡ The operation of heating this residue (which contains nitrate of potassa) with hydrochloric acid, must not be conducted in a platinum dish.

In the fluid filtered from the sulphide of manganese, there still remains the lithia to be determined. To effect the determination of this substance, mix the filtrate with ammonia and carbonate of ammonia, allow to deposit, and filter the fluid from the carbonate of lime and baryta. Evaporate the filtrate to dryness, and remove the chloride of ammonium by gentle ignition; then, to remove the magnesia, boil the residue with water, with addition of a little pure milk of lime, filter, remove the excess of lime, cautiously, with ammonia, carbonate and some oxalate of ammonia, filter, evaporate the filtrate to dryness, remove the ammonia salts by ignition, and treat the residue with a mixture of absolute alcohol and anhydrous ether, with addition of a few drops of hydrochloric acid.* If chloride of lithium is present, it will dissolve in this mixture. Evaporate the solution, dissolve the residue in water, and test the moderately concentrated solution with ammonia and carbonate of ammonia. If the slightest turbidity is perceptible, the same operation must be repeated, to remove the still remaining traces of baryta, lime, or magnesia. Evaporate again to dryness, ignite gently, treat the residue once more with absolute alcohol and ether, with addition of a little hydrochloric acid, and filter if anything is left undissolved; evaporate the solution, and determine the lithia finally as directed § 152 (7).

8. Estimation of the Ammonia.

To effect the estimation of the ammonia in mineral waters, I can recommend the following method, which I have employed with good results in my analysis of the Wiesbaden *Kochbrunnen*:—

Evaporate about 2000 grammes of the mineral water, with addition of a small measured amount of dilute hydrochloric acid, in a tubulated retort, until only a small quantity of the fluid is left. Add to this, through a funnel-tube, a measured quantity of freshly prepared solution of soda, put the neck of the retort a little upwards, and keep the contents boiling until the fluid is almost entirely evaporated. Conduct the whole of the vapors escaping through a *Liebig's* condensing apparatus, and receive the distillate in a flask containing a little water acidified with a small measured quantity of hydrochloric acid. Convert the chloride of ammonium contained in this fluid into ammonio-bichloride of platinum, by evaporation with a measured quantity of bichloride of platinum (§ 99, 2). Make now a counter-experiment with the same quantities of hydrochloric acid, solution of soda, and bichloride of platinum, and deduct the small amount of ammonio-bichloride of platinum obtained in this, from that found in the first experiment: the difference expresses the quantity proceeding from the analysed water.

Instead of this method, you may also employ the more simple process which *Boussingault* has lately proposed ("Compt. rend.," 36, 814; "Pharm. Centralblatt," 1853, 369), and which is conducted as follows:—

Distil, in a distilling apparatus, about 10 litres of the water, until about $\frac{2}{3}$ have passed over. In the analysis of saline springs, you must add some solution of soda or milk of lime to ensure the ammonia passing over. Transfer the distillate to a glass flask connected with a *Liebig's* condensing apparatus, and distil ½ over. Determine the ammonia in this distillate by adding 5 or 10 c.c. of very dilute sulphuric acid, and saturating the excess of the latter by a solution of soda, of which 5 c.c. neutralize 1 c.c. of the dilute sulphuric acid used (comp. § 99, 3). Let another ½ distil over, and determine the ammonia in this (if any is still present) in the same way. But the first portion usually contains the whole of the ammonia.

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* Chloride of lithium is rendered basic even by gentle ignition, § 152 (7).

9. DETERMINATION OF THE NITRIC ACID.

Evaporate a rather large quantity of the water with an excess of pure carbonate of soda, filter the precipitate formed, wash, evaporate the filtrate to dryness, mix the residue uniformly, weigh, and determine in weighed portions of it the nitric acid by *Pelouze's* method modified by me (§ 149, II., *a*).

10. DETECTION AND ESTIMATION OF THE CRENIC AND APOCRENIC ACIDS.

Boil a rather large quantity of the precipitate formed upon the evaporation of the water, about 1 hour, with solution of potassa; filter, acidify the filtrate with acetic acid, add ammonia, and, after 12 hours, filter off the precipitate of silicic acid and alumina, which usually forms. Add to the filtrate acetic acid to acid reaction, then neutral acetate of copper. If a brownish precipitate forms, this consists of apocrenate of copper (which, according to *Mulder*, contains variable quantities of ammonia); an analysis of apocrenate of copper dried at 284° F., gave 42·8 per cent. of oxide of copper. Mix the fluid filtered from the precipitate with carbonate of ammonia, until the green color is changed to blue; then apply a gentle heat. If a bluish-green precipitate forms, this is crenate of copper, which, dried at 284° F., contains 74·12 per cent. of oxide of copper (*Mulder*).*

11. DETECTION AND ESTIMATION OF OTHER NON-VOLATILE ORGANIC MATTERS.

Almost all mineral waters contain non-volatile organic matters, even though only in very small proportions. Many of them are of a resinous nature, in which case they pass into the alcoholic solution of the residue of the mineral water; from this solution they separate upon distillation, with addition of some water in the last stage of the process. If present, they may be quantitatively determined, on the occasion of the estimation of the iodine and bromine (§ 209, 7, *a*). Another class of organic matters do not dissolve in alcohol, but are obtained in solution, if the residue of the mineral water is boiled with water. If it is wished to determine the weight of these organic matters, which are usually, for want of a more accurate knowledge of their nature, called extractive matters, the aqueous extract of the residue of the mineral water, exhausted by alcohol, is evaporated with carbonate of soda to dryness, the residue boiled with water, the solution filtered, the filtrate evaporated to dryness, and the residue dried at 284° F., until it suffers no further diminution of weight. It is then gently ignited until the black color which it at first acquires has disappeared. The difference between the weight of the dried and that of the ignited residue indicates the amount of the extractive matter. Small quantities of organic matters are occasionally still left in the residue of the mineral water after exhausting with alcohol and with water. If it were attempted to determine these by the difference between the weight of the residue dried at 284° F., and that of the ignited residue, a very inaccurate result would be arrived at, as, under these circumstances, to name only one source of error, carbonate of magnesia loses its carbonic acid.

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* For more detailed information on the subject of crenic acid and apocrenic acid, I refer to *Mulder's* paper on these acids in the "Journal f. prakt. Chem.," 32, p. 321.

12. Detection and Estimation of Volatile Organic Acids.

Scherer ("Annal. d. Chem. u. Pharm.," 99, 257) found, in his analysis of the mineral springs of Brückenau, in Bavaria, also butyric acid, propionic acid, acetic acid, and formic acid—substances which had not before been observed in mineral waters. Soon after, I also found traces of the same acids in the sulphur spring of Weilbach ("Journ. f. prakt. Chem.," 70, 15). If it is intended to examine a mineral water for these acids, the water must be used quite fresh, since otherwise the volatile organic acids detected afterwards might be products of subsequent processes of decomposition. The following is *Scherer's* process for determining these volatile organic acids :—

Evaporate a rather large quantity of the mineral water, and filter the fluid off from the precipitate formed ; if the water contains no alkaline bicarbonate, add carbonate of soda to alkaline reaction, before proceeding to evaporate. Acidify the concentrated mother-liquor with sulphuric acid, with proper caution, and precipitate the chlorine by sulphate of oxide of silver, taking care to have rather a slight excess of chlorine than of silver. Filter, distil the filtrate until the fluid passing over no longer shows acid reaction, saturate the distillate with baryta water, remove any excess of baryta by carbonic acid, boil, concentrate, filter, evaporate to dryness, in a weighed dish, dry at 212° F., and weigh the residue, which contains the volatile organic acids in combination with baryta. Extract the residue with warm spirit of wine, which leaves the formate of baryta undissolved. After drying and weighing the latter, test it with solution of nitrate of silver and chloride of mercury. Evaporate the alcoholic solution of the other baryta compounds at a gentle heat, dissolve the larger portion of the residue in a copious amount of water, and precipitate the baryta from the solution by sulphate of oxide of silver, with proper caution. Let the fluid filtered off from the precipitate evaporate under the exsiccator. As soon as a sufficient quantity of silver salt has crystallized, remove the crystals from the fluid, dry over sulphuric acid, and employ the dry salt for the determination of the equivalent. Evaporate finally the rest of the fluid over sulphuric acid, press the salt between sheets of blotting paper, dry over sulphuric acid, and analyse the salt.

By way of control, determine, by means of sulphuric acid, the baryta in another portion of the residue left upon the evaporation of the alcoholic solution of the baryta salts. In this process the presence of the volatile fatty acid (propionic acid, butyric acid, &c.) may be detected by the characteristic odor of the acid. If the fluid is sufficiently concentrated, and has been allowed to stand at rest for some time, the microscope will also occasionally show minute fatty drops floating on the surface.

13. As regards BORACIC ACID and FLUORINE,* the simple detection of these substances is generally sufficient for the purposes of the analysis of a mineral water. For their quantitative determination in exceptional cases, I refer to the General Part.

14. EXAMINATION OF THE GASES.

§ 210.

To examine the gases collected at the spring (see § 208, 11 and 12), and brought to the laboratory in sealed tubes, take a graduated tube of the form described in § 12, and illustrated in Fig. 2, moisten the inside with a drop of water, and then fill with mercury.† Immerse the tube containing the gas in the mercurial trough, break off the point, and, by giving the proper inclination, cause the gas to ascend into the graduated tube. Read off the volume of the gas, with due regard to the temperature and atmospheric pressure; then introduce into the gas, by means of a platinum wire, on which it is cast, a ball of hydrate of potassa,‡ moistened with water. Take care not to allow the other end of the wire to project above the surface of the mercury, otherwise a diffusion of the confined gas with the atmospheric air will take place along the wire, which is not moistened by the mercury. When the volume of the gas shows no further diminution, replace the moist potassa ball by a dry one, remove this also after an hour, and then read off the volume of the gas. The gas absorbed consists of carbonic acid, and, in cases where sulphuretted hydrogen is present, also of the latter gas, which, however, has already been determined; still, the sulphide of potassium in the potassa ball may be estimated as directed § 148, II., 2, *c*.

The gaseous residue consists usually only of oxygen and nitrogen, in which case it may be examined as directed in the chapter on the Analysis of Atmospheric Air (§ 267). If there is reason to suspect the presence of marsh gas, the oxygen is removed by means of a well-wetted ball of phosphorus‖ introduced into the gaseous mixture, and left in contact with it in a moderately warm place, as long as white fumes of phosphorous acid are visible round the ball. If no fumes are visible at 59—77° F., this must not be looked upon as a proof of the absence of oxygen, as the presence of carbides of hydrogen prevents the slow combustion of the phosphorus. In such cases, the phosphorus ball occasionally requires heating near to the fusing point, to bring about the absorption of the oxygen (*Bunsen*). The phosphorous acid fumes, the tension of which cannot well be taken into account, are ultimately absorbed by a moistened potassa ball; the gas is then dried by means of a ball of hydrate of potassa, and finally measured in the dry state. Instead of a phosphorus ball, a ball of papier-mâché may be employed to effect the removal of the oxygen; this papier-mâché ball must be moistened with a concentrated alkaline solution of pyrogallate of potassa, and, if required, be replaced, after some time, by a second ball. After this operation, the gas is dried by means of a ball of hydrate of potassa. *Bunsen* prefers the use of a papier-mâché instead of a phosphorus ball. The composition of the gaseous residue, which generally consists either of nitrogen alone, or of nitrogen plus marsh gas, is now ascertained by transferring it, wholly or partially, to a eudiometer (§ 12, Fig. 1), mixing with 8—12 vols. of air and 2 vols. of oxygen—to guard against the formation of nitric acid—and trying to explode the gaseous mixture. Should this fail, electrolytic detonating gas is added to the extreme limit of combustibility, the carbonic acid generated re-absorbed, the marsh gas calculated from this, and the nitrogen found by the difference. For the details of the process, I refer to *Bunsen's* "Gasometry," translated by Roscoe, a work which ought to be in the hands of every one engaged in the analysis of gases.

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* For the detection of fluorine, compare *J. Nicklès* ("Compt. rend.," 1857, 44, 679; "Journ. f. prakt. Chem.," 71, 383). *Nicklès* recommends to free the sulphuric acid most carefully from fluorine before using it, and to substitute a plate of rock crystal for the glass plate usually employed.

† See § 184, *aa*, footnote.

‡ Which, besides the hydration water, contains also still water of crystallization. Balls of this kind are made by pouring fused crystallized hydrate of potassa into a bullet-mould of about six millimetres inner diameter, into which a platinum wire is inserted, with the end reaching into the middle. After cooling, the ball is found attached to the wire. The neck which has formed on the wire is scraped off with a knife.

‖ Cast on a platinum wire, under warm water.

To ascertain whether the gaseous residue left after the absorption of the carbonic acid and the oxygen, contains carburetted hydrogen, I have often successfully employed the following method: Insert one limb of a U-shaped narrow glass tube into the cylinder containing the gaseous residue, which is confined over water; connect the other limb with a piece of india-rubber tubing, closed by means of a valve. Arrange now the following apparatus:—

Pour some solution of potassa into a small U-shaped tube, connect the outer limb of this with a little tube bent at a right angle, which bears a small piece of india-rubber tubing closed by a compression clamp. Connect the other limb with a second small U-shaped tube, filled with hydrate of potassa, and this again with a thin combustion tube, 2 decimetres long, filled in the middle with a rather close-packed layer, about 8 centimetres long, of fine copper turnings strongly oxidized by ignition in oxygen gas. Connect the other end of the combustion tube with a somewhat larger U-shaped tube, containing lime water, and this again with a hydrate of potassa tube; connect the latter finally with an aspirator. Open the cock of the latter, and observe whether the joinings are air-tight; if they are, heat the copper turnings, by means of two gas lamps, to ignition, open the compression clamp cautiously, and let a slow current of air pass through the apparatus for 5 minutes. This should not impart the least turbidity to the lime water; if the lime water is rendered turbid, replace it by a fresh portion, after the first ignition, and repeat the experiment. If the lime water remains clear, connect, by means of a small glass tube, the india-rubber tubing which is closed by a valve, with that closed by a compression clamp. As the former, which closes the bent tube inserted into the cylinder, remains closed, no more air bubbles can pass through the apparatus. Open now the valve a little, and allow the gas of the cylinder to enter very slowly. The quantity of gas is generally so small that it is entirely absorbed in the first U-shaped tube. When all the gas is absorbed, allow also some water to enter, and close the valve only when the water just makes its appearance in the little glass tube behind it. Now close the clamp, disconnect the india-rubber tube with the valve, and, opening the clamp a little, allow a very slow current of air to pass for a sufficient length of time over the ignited oxide of copper. This current of air carries along with it the gas which has previously entered; if this contains carburetted hydrogen, the lime water is rendered turbid, owing to the formation of carbonate of lime. If the turbidity is sufficiently marked, the quantity of the carbonate of lime may be determined, and the amount of marsh gas calculated from the result.

MODIFICATIONS REQUIRED BY THE PRESENCE OF A FIXED ALKALINE CARBONATE.

§ 211.

1. A mineral water containing an alkaline carbonate, cannot contain *soluble* salts of lime and magnesia; all the lime and magnesia found in it must, therefore, be regarded as carbonates dissolved by the agency of free carbonic acid, although the whole of the magnesia does not precipitate upon boiling the water, a small quantity of a double carbonate of soda and magnesia being invariably formed under these circumstances. The separate determination of the lime and magnesia in the precipitate subsiding upon the ebullition of the water, and in the boiled water, is therefore dispensed with. However, if desirable, these substances may be determined according to the directions of § 209.

2. In the analysis of a water so highly dilute that a preliminary concentration is required, before the estimation of the chlorine and the sulphuric acid can be effected, I recommend the following method :—

1. ESTIMATION OF THE CHLORINE, PROTOXIDE OF IRON, PROTOXIDE OF MANGANESE, LIME, AND MAGNESIA.

Transfer the water of several weighed bottles (together about 2000 grammes) to a porcelain dish; rinse the bottles, and add the rinsings to the water in the dish. A precipitate of sesquioxide of iron may have formed in the bottles; it is a matter of indifference whether the rinsing removes this completely or not. Evaporate the water to $\frac{1}{6}$; pass the concentrated fluid through a filter thoroughly washed with some nitric acid and water, and well wash the precipitate with boiling water.

a. Acidify the *filtrate* with nitric acid, precipitate with nitrate of silver, filter, and determine the chloride of silver in the usual way. Free the filtrate from the excess of silver by means of hydrochloric acid, evaporate, and then throw down, with oxalate of ammonia and phosphate of soda, the small quantity of magnesia which is never absent, and the minute traces of lime which may be present. (The precipitates are ignited and weighed with the principal quantities.)

b. Dissolve the *precipitate*, together with the residuary sediment which may still remain in the bottles, in hydrochloric acid, and treat the solution by one of the methods given in § 209, 4.

2. ESTIMATION OF THE SILICIC ACID, THE SULPHURIC ACID, AND THE ALKALIES.

Evaporate the contents of several weighed bottles in a porcelain dish; pour a little hydrochloric acid into the bottles, to dissolve the deposit of sesquioxide of iron, &c., which may have formed in them, and add the solution to the contents of the dish. Continue to evaporate the now acid fluid for some time longer, then transfer to a platinum dish, and evaporate to dryness on the water-bath. Moisten the residue with hydrochloric acid, and evaporate again to dryness; moisten once more with hydrochloric acid, add water, apply heat, and filter off the *silicic acid.*

Precipitate the filtrate with chloride of barium, added in the least possible excess, and filter the fluid from the *sulphate* of baryta. Evaporate the filtrate nearly to dryness, dissolve the residue in water, and cautiously add *pure* milk of lime until the fluid manifests a strongly alkaline reaction. Heat, and filter; precipitate with ammonia and carbonate of ammonia, and filter again; evaporate the filtrate to dryness, in a platinum dish, and gently ignite the residue until all salts of ammonia are expelled. Dissolve the residue in a little water, precipitate again with ammonia and carbonate of ammonia, filter, evaporate, weigh the now pure chlorides of the alkali metals, and separate potassa and soda as directed § 152.

The quantity of the alkaline carbonate is determined best in the indirect way, in the calculation of the results—provided always the various analytical processes have been carefully conducted.—Of the direct methods proposed, I will give the following:—

a. Boil 300—400 grammes of the water for some time, filter, and wash the precipitate with hot water. Mix the filtrate intimately with the washings, divide the mixture into two equal parts, and determine in one the chlorine in the usual way, after previous addition of nitric acid. Mix the other half with pure hydrochloric acid until the fluid distinctly manifests an acid reaction; evaporate to dryness, and gently ignite the residue; then dissolve in water, filter, and determine the chlorine also in this solution. It is evident that you will obtain in this second operation more chlorine than in the first: each equivalent of chlorine by which the result of the second operation exceeds that of the first, corresponds to 1 equivalent of carbonic acid which existed in combination with an alkali. This method gives a little too much, as the original filtrate always contains some carbonate of soda and magnesia. If you wish to correct this error, determine the small quantity of magnesia which existed as chloride of magnesium in the fluid precipitated with solution of nitrate of silver, and deduct from the difference between the two determinations of the chlorine, an amount of the latter substance corresponding to the magnesia. The carbonate of soda must not be converted into chloride of sodium by evaporating the solution with chloride of ammonium; since the excess of the chloride of ammonium would decompose the alkaline sulphate present, and more chlorine would accordingly be found than corresponds to the alkaline carbonate.

b. Proceed at first as in *a*, but use double the quantity of water, and divide the filtrate and washings into two equal, or, at least, measured parts. Strongly concentrate one part, and determine the carbonated alkali (together with the trace of lime and the minute quantity of magnesia present) volumetrically, as directed § 220; in the other part determine the lime and magnesia which may be present; this will serve to correct the result of the alkalimetric analysis of the first part, since carbonate of lime and carbonate of magnesia exercise, of course, the same neutralizing action upon acids as an equivalent amount of carbonate of soda.

REMARKS ON THE ANALYSIS OF SULPHURETTED WATERS.

§ 212.

We have already seen, in §§ 208-9, that the sulplur in sulphuretted waters may be present in different forms of combination, and what are the best methods to employ for determining the free sulphuretted hydrogen, as well as the sulphuretted hydrogen existing in combination with a metallic sulphide, in form of a sulphur salt; also the sulphur present in form of metallic sulphide or bi-sulphide, and, lastly, the hyposulphurous acid which may be present.

I deem it advisable to add a few remarks and observations made by me and others.

1. *The determination of the sulphuric acid* cannot be effected in the usual way, as the sulphuretted hydrogen is constantly undergoing oxidation by the oxygen of the air, which must of necessity lead to serious errors. The sulphuric acid in sulphuretted mineral waters should therefore be estimated as directed § 167 (205).

2. *The total amount of the sulphur* present in a mineral water, in whatever form of combination—whether with oxygen, hydrogen, or metals—is estimated, by way of control, by conducting into a measured quantity of the water chlorine gas free from air, and precipitating the sulphuric acid formed with chloride of barium.

3. The deportment of mineral waters containing free sulphuretted hydrogen differs of course from that of waters containing principally metallic sulphides, or sulphur salts (hepatic waters). As an illustration of waters of the *former description*, I may mention the water of *Weilbach*, in which nearly the whole of the sulphur which is not combined with oxygen is present as free sulphuretted hydrogen. The water smells strongly of this gas; when shaken in a half-filled bottle, it evolves sulphuretted hydrogen along with carbonic acid; upon transmission of hydrogen it completely loses the sulphuretted hydrogen, retaining, at most, only inappreciable traces. When kept in a bottle containing air, sulphur speedily separates, the fluid turning turbid, or depositing a precipitate, whilst the smell of sulphuretted hydrogen becomes fainter and fainter; after some time, the continued action of the air generally oxidizes the separated sulphur to sulphuric acid, which dissolves, leaving the water again as clear as at first.

As an illustration of waters of the *latter description*, may be mentioned the water of *Stachelberg*, analysed by *Simmler* ("Journ. f. prakt. Chem.," 71, 1). This water smells only very slightly, and in winter scarcely at all, of sulphuretted hydrogen; a minute's action of it upon reddened litmus paper restores the blue colour of that reagent.; it leaves turmeric paper unaltered. Protochloride of manganese produces in it a carnation, sulphate of protoxide of iron a black precipitate. Nitro-prusside of sodium imparts to it a reddish violet tint. If a bottle is filled with the water, the latter soon turns slightly turbid; after about five minutes it recovers its original clearness, but the color is now distinctly yellowish. Upon further access of air, renewed turbidity is observed, followed again by clearing, after which the water is found to have acquired a deep yellow tint, owing to the formation of bisulphide. With full access of air, a copious precipitate of sulphur finally subsides, hyposulphite of soda being formed at the same time.

The cause of the different deportment of these two mineral waters is to be found in the different proportion which the sulphur respectively contained in them, in combination with hydrogen or metals, bears to the free carbonic acid present, which is as 1 : 24 in the water of *Weilbach*, and only as 1 : 2 in that of *Stachelberg*. If a current of carbonic acid were conducted into the latter, this would convert most of the sulphur of the sulphides in the water into free sulphuretted hydrogen; since carbonic acid expels sulphuretted hydrogen from sulphide of sodium or hydrated sulphide of sodium, as, on the other hand, sulphuretted hydrogen expels carbonic acid from bicarbonate of soda.

Owing to these slight differences of affinity, the action depends upon the amount present of either body; the larger, therefore, the amount of free carbonic acid in a water containing carbonate of soda, the smaller will be the quantity of sulphuretted hydrogen in a state of combination, and the larger that of free sulphuretted hydrogen. The temperature also exercises some influence in the matter; thus, for instance, bicarbonate of soda may exist in the cold in the presence of sulphide of sodium, whilst at a higher temperature simple carbonate will form, with disengagement of sulphuretted hydrogen. Sulphuretted waters containing no alkaline bicarbonates, which accordingly acquire no alkaline reaction upon boiling, are looked upon as simple solutions of sulphuretted hydrogen; the sulphuretted water of *Sandefjord*, analysed by *A.* and *H. Strecker*, belongs to this class ("Annal. d. Chem. u. Pharm.," 95, 175).

CALCULATION, CONTROL, AND ARRANGEMENT OF THE RESULTS OF ANALYSES OF MINERAL WATERS.

§ 213.

The results of the several analytical processes described in 1, are obtained by direct experiments. They are altogether independent of any theoretical views which may be entertained as to the manner in which the several constituents are combined or associated with each other.

As our theoretical views on the subject may change with the progress of chemistry, it is absolutely indispensable, in reports of analyses of waters, to give the direct results obtained, and the methods by which they were obtained. An analysis so recorded is of service for all times, as it supplies, at least, the requisite data to determine whether the composition of a water is constant or not.

With respect to the principles that guide chemists in the hypothetical association of the acids and bases found in the water, it is assumed that the combination of these bases and acids is governed by their respective affinities, *i. e.*, the strongest acid is assumed to be combined with the strongest base, &c.; due attention being paid, however, also, to the greater or less degree of solubility of the salts, since it is well known that this exercises a considerable influence upon the manifestations of the force of affinity. Thus, for instance, when lime, potassa, and sulphuric acid are found in the boiled water, the sulphuric acid is assumed to exist, in the first place, in combination with the lime, &c. It cannot be denied, however, that this way of proceeding leaves much to the individual views and discretion of the analyst, and, consequently, that different modes of associating the several ingredients found may lead to different results for one and the same analysis.

A general understanding upon this point would be very advantageous, because without it the comparison of two mineral waters is beset with difficulties. As long as an agreement of this kind is wanting, a comparison between two mineral waters can only be made as regards the direct and immediate results of the respective analyses.

One point, I think, should be at once agreed upon, viz., to put all the salts down in the calculation as anhydrous salts.

To illustrate the principles which I conceive ought to guide chemists in this matter, and also the way of controlling the results obtained, I select the following example:—

ANALYSIS OF THE BONIFACE WELL AT SALZSCHLIRF.*

a. Direct Results of the Analysis in per Cents.

SPECIFIC GRAVITY = 1·011164.

1. TOTAL AMOUNT OF THE FIXED CONSTITUENTS: 1·3778 per cent.

2. JOINT AMOUNT OF CHLORINE, IODINE, AND BROMINE: 2·8071 per cent. silver precipitate.

3. TOTAL AMOUNT OF LIME, MAGNESIA, IRON, AND SILICIC ACID:

a. Lime 0·10442 per cent.
b. Silica 0·00114 per cent.

(The gross amount of magnesia and iron was not determined.)

4. *α.* LIME, MAGNESIA, AND IRON IN THE PRECIPITATE WHICH SEPARATES UPON BOILING:

a. Lime 0·03642 per cent.
b. Magnesia 0·00041 per cent.
c. Sesquioxide of iron 0·00066 per cent.

β. LIME AND MAGNESIA IN THE BOILED AND FILTERED WATER.

a. Lime 0·064724 per cent.
b. Magnesium 0·028855 per cent.

5. ALKALIES:

a. Potassa 0·00865 per cent.
b. Soda 0·54783 per cent.

6. SULPHURIC ACID: 0·10853 per cent.

7. TOTAL AMOUNT OF CARBONIC ACID: 0·194301 per cent.

8. BROMINE AND IODINE:

a. Bromine 0·000402 per cent.
b. Iodine 0·000447 per cent.

The remaining constituents, such as lithia, phosphoric acid, protoxide of manganese, crenic acid, apocrenic acid, and extractive matter, were not determined by weight.

b. Calculation of the Results.

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* Compare Chemical Investigations of the Mineral Spring at Salzschlirf in the Bishopric of Fulda (Electorate of Hesse), by *Fresenius* and *Will*, "Annalen der Chemie and Pharmacie," LII. 66. To facilitate references to the original paper, I have copied the results as they stand, and have refrained from altering them according to the corrected equivalents.

α. The salts precipitated upon boiling are assumed to be present as carbonates held in solution by free carbonic acid.

1. 0·00066 sesquioxide of iron correspond to 0·00096 of CARBONATE OF PROTOXIDE OF IRON, which contain 0·00038 of carbonic acid.
2. 0·03642 of lime correspond to 0·06533 of CARBONATE OF LIME, which contain 0·02891 of carbonic acid.
3. 0·00041 of magnesia correspond to 0·00085 of CARBONATE OF MAGNESIA ($Mg\,O, C\,O_2$), which contain 0·00044 of carbonic acid.

β. The amount of carbonic acid present in the free state, and in combination with carbonates (in the form of bicarbonates), may now be readily calculated by subtracting the amount of the acid in the carbonates, from the total weight of the carbonic acid found in the analysed water, viz.,

Total amount of the carbonic acid . . .		0·194301
Carbonic acid existing in combination		
With lime . . .	0·02891	
With magnesia . .	0·00044	
With protoxide of iron .	0·00038	
Total		0·029730
There remain FREE and SEMI-COMBINED CARBONIC ACID		0·164571

γ. The sulphuric acid is assumed to exist, in the first place, in combination with lime; should an excess remain, this is assumed to exist in combination with potassa, and should there still remain an excess, this is supposed to exist as sulphate of soda.

1. The boiled water contains 0·064724 of lime, which combine with 0·09261 of sulphuric acid, giving 0·15733 of SULPHATE OF LIME.
2. 0·00865 of potassa combine with 0·00737 of sulphuric acid, giving 0·01602 of SULPHATE OF POTASSA.
3. Total amount of sulphuric acid present . . 0·10853

Of which there are combined		
With lime	0·09261	
With potassa . . .	0·00737	
Total		0·09998
There remain		0·00855

of sulphuric acid, which combine with 0·00666 of soda, giving 0·01521 of SULPHATE OF SODA.

δ. The rest of the soda present exists as chloride of sodium.

Total amount of soda present . . .	0·54583
Combined with sulphuric acid . .	0·00666
There remain	0·53917

of soda, which correspond to 0·40123 of sodium, which latter, combining with 0·61040 of chlorine, give 1·01163 of CHLORIDE OF SODIUM.

ε. The iodine and bromine are assumed to exist in combination with magnesium; and the rest of the magnesium as chloride of magnesium.

1. 0·000447 of iodine combine with 0·000044 of magnesium, giving 0·000491 of IODIDE OF MAGNESIUM.

2. 0·000402 of bromine combine with 0·000065 of magnesium, giving 0·000467 of BROMIDE OF MAGNESIUM.

Total amount of magnesium contained in the boiled water : 0·028855
Of which there are combined

With iodine	0·000044	
With bromine	0·000065	
Total		0·000109
There remain		0·028746

of magnesium, which are combined with 0·080220 of chlorine, givi 0·108966 of CHLORIDE OF MAGNESIUM.

c. Control.

I. The joint amount of the lime in the boiled water and in the precipitate which forms upon ebullition must be equal or, at least, nearly so to the total amount of the lime.

Total amount of lime		0·10442
Combined with carbonic acid	0·03642	
Combined with sulphuric acid	0·06472	
Total		0·10114

II. The amount of chlorine directly determined must correspond to the joint amount of the chlorine contained in the chlorides of sodium and magnesium.

The joint amount of the chloride, bromide, and iodide of silver is		2·807100
Subtract from this amount of iodide of silver corresponding to 0·000491 of iodide of magnesium, viz.	0·000828	
And the amount of bromide of silver corresponding to 0·000467 of bromide of magnesium, viz.	0·000958	
Total		0·001786
There remain		2·805314
which correspond to chlorine		0·69202
According to δ	0·61040 of chlorine are combined with sodium.	
And according to ε	0·08022 of chlorine are combined with magnesium.	
Total		0·69062

III. The total amount of the fixed constituents must correspond to the joint amount of the several ingredients (the iron is here calculated as sesquioxide, since it is contained in that form in the residue).

Total amount of the fixed constituents = 1·37780

The respective estimations of the several constituents gave:

Carbonate of lime	0·06533
" magnesia	0·00085
Sulphate of lime	0·15733
" potassa	0·01602
" soda	0·01521
Chloride of sodium	1·01163
" magnesium	0·10896
Iodide of magnesium	0·00049
Bromide of magnesium	0·00047
Sesquioxide of iron	0·00066
Silica	0·00114
Total	1·37890*

d. Arrangement and Classification of the Results.

The analyst should state, in the first place, how many parts of the several constituents are contained in 100 or, better, in 1000 parts of the water; and, in the second place, how many grains (1 lb. = 7680 grs.) of the several constituents are contained in 1 pound of the water.

The most appropriate way of classifying the results, is to enumerate them under the following heads:—

A. FIXED CONSTITUENTS.

a. Present in ponderable quantity.
b. Present in imponderable quantity.

B. VOLATILE CONSTITUENTS.

As regards the carbonates, it is a question whether they should be put down as neutral salts, the excess of carbonic acid being considered partly as forming bicarbonates, and partly as free acid; or whether they should be calculated at once as bicarbonates, the excess of the carbonic acid being deemed to be present in the free state. Chemists sometimes adopt the one way, sometimes the other, but the former more frequently than the latter. I generally arrange the results of my analyses of mineral waters both ways, to facilitate comparison with the results of the analyses of similar springs.

Besides stating the weight of the carbonic acid (and of the gases in general), it is customary to give also the volumes, calculated both in cubic centimetres and in cubic inches (1 lb. of water = 32 cubic inches). These calculations are adjusted to the temperature of the spring.

For similar examples to guide the young chemist in calculating and controlling the results of analyses of mineral waters, I refer to the following papers, contained in my work on the analysis of the most important mineral springs of the Duchy of Nassau, "Chemische Untersuchungen der wichtigsten Mineralwasser des Herzogthums Nassau, von Professor Dr. *R. Fresenius*," published by *Kreidel* and *Niedner*, at Wiesbaden, from 1850—1857; also in "Jahrbücher des nassauischer naturhistorischen Vereins," vols. 6—12.

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* This control gives properly corresponding results only in the analysis of waters containing but small quantities of carbonate of magnesia, chloride of magnesium, and silicic acid, for the reasons stated § 205, 7. In cases where these constituents are present in large proportions, it is advisable to make, instead of or besides this control, a comparison of the sulphates (the iron being estimated as pure sesquioxide) with the residue obtained by evaporating the water with sulphuric acid and igniting (§ 209, 1).

1. Analysis of the *Kochbrunnen* of Wiesbaden (hot saline springs).
2. Analysis of the mineral springs of Ems (thermal alkaline spring).
3. Analysis of the springs of Schlangenbad (thermal springs holding only an extremely small quantity of solid constituents in solution).
4. Analysis of the mineral springs of Langenschwalbach (alkaline chalybeate springs, abounding in carbonic acid).
5. Analysis of the sulphuretted spring of Weilbach (cold hydrosulphuretted spring).
6. Analysis of the mineral spring of Geilnau (alkaline chalybeate spring, abounding in carbonic acid).

Papers 4, 5, and 6, have also been published in the "Journ. f. prakt. Chem.," vols. 64, 70, 72.

Papers 1 and 2 contain also a detailed description of the methods employed to determine the muddy ochreous and the solid sinter deposits of these springs.

II. ANALYSIS OF SOME OF THE MORE IMPORTANT TECHNICAL PRODUCTS AND MINERALS EMPLOYED IN THE ARTS, &c., WITH PROCESSES FOR ESTIMATING THEIR COMMERCIAL VALUE.

1. Determination of the Amount of Anhydrous Acid in Solution (Acidimetry).

A. Estimation by Specific Gravity.

§ 214.

The specific gravity of an acid of course varies with the degree of its dilution. Tables, based upon the results of exact experiments, have been drawn up, expressing in numbers the relation between the specific gravity of the aqueous solution of an acid, and the amount of anhydrous acid contained in it. Therefore, to know the amount of anhydrous acid contained in an aqueous solution of an acid, it suffices, in many cases, simply to determine its specific gravity. Of course the acids must, in that case, be perfectly or at least nearly free from admixtures of other substances dissolved in them. Now, as most acids are volatile (sulphuric acid, hydrochloric acid, nitric acid, acetic acid), any non-volatile admixture may be readily detected by evaporating a sample of the acid in a small platinum or porcelain dish.

The determination of the specific gravity is effected either by comparing the weight of equal volumes of water and acid (§ 209), or by means of a good hydrometer. The results must, of course, be adjusted to the temperature to which the Tables refer.

The following Tables give the relations between the specific gravity and the amount of anhydrous acid, for sulphuric acid, hydrochloric acid, nitric acid, and acetic acid.

TABLE I.

Specific gravity of SULPHURIC ACID of different degrees of dilution, by *Bineau;* calculated for 15° C. (59° F.), by *Otto.*

Hydrated acid.	Specific gravity.	Anhydrous acid.	Hydrated acid.	Specific gravity.	Anhydrous acid.
100	1·8426	81·63	50	1·398	40·81
99	1·842	80·81	49	1·3886	40·00
98	1·8406	80·00	48	1·379	39·18
97	1·840	79·18	47	1·370	38·36
96	1·8384	78·36	46	1·361	37·55
95	1·8376	77·55	45	1·351	36·73
94	1·8356	76·73	44	1·342	35·82
93	1·834	75·91	43	1·333	35·10
92	1·831	75·10	42	1·324	34·28
91	1·827	74·28	41	1·315	33·47
90	1·822	73·47	40	1·306	32·65
89	1·816	72·65	39	1·2976	31·83
88	1·809	71·83	38	1·289	31·02
87	1·802	71·02	37	1·281	30·20
86	1·794	70·10	36	1·272	29·38
85	1·786	69·38	35	1·264	28·57
84	1·777	68·57	34	1·256	27·75
83	1·767	67·75	33	1·2476	26·94
82	1·756	66·94	32	1·239	26·12
81	1·745	66·12	31	1·231	25·30
80	1·734	65·30	30	1·223	24·49
79	1·722	64·48	29	1·215	23·67
78	1·710	63·67	28	1·2066	22·85
77	1·698	62·85	27	1·198	22·03
76	1·686	62·04	26	1·190	21·22
75	1·675	61·22	25	1·182	20·40
74	1·663	60·40	24	1·174	19·58
73	1·651	59·59	23	1·167	18·77
72	1·639	58·77	22	1·159	17·95
71	1·637	57·95	21	1·1516	17·14
70	1·615	57·14	20	1·144	16·32
69	1·604	56·32	19	1·136	15·51
68	1·592	55·59	18	1·129	14·69
67	1·580	54·69	17	1·121	13·87
66	1·578	53·87	16	1·1136	13·06
65	1·557	53·05	15	1·106	12·24
64	1·545	52·24	14	1·098	11·42
63	1·534	51·42	13	1·091	10·61
62	1·523	50·61	12	1·083	9·79
61	1·512	49·79	11	1·0756	8·98
60	1·501	48·98	10	1·068	8·16
59	1·490	48·16	9	1·061	7·34
58	1·480	47·34	8	1·0536	6·53
57	1·469	46·53	7	1·0464	5·71
56	1·4586	45·71	6	1·039	4·89
55	1·448	44·89	5	1·032	4·08
54	1·438	44·07	4	1·0256	3·26
53	1·428	43·26	3	1·019	2·445
52	1·418	42·45	2	1·013	1·63
51	1·408	41·63	1	1·0064	0·816

TABLE II.

Specific gravity of dilute Hydrochloric Acid containing different proportions of hydrochloric acid gas, by *Ure*. Temperature 15° C. (59° F.)

Specific gravity.	Hydrochloric acid gas.	Specific gravity.	Hydrochloric acid gas.
1·2000	40·777	1·1000	20·388
1·1982	40·369	1·0980	19·980
1·1964	39·961	1·0960	19·572
1·1946	39·554	1·0939	19·165
1·1928	39·146	1·0919	18·757
1·1910	38·738	1·0899	18·349
1·1898	38·330	1·0879	17·941
1·1875	37·923	1·0859	17·534
1·1857	37·516	1·0838	17·126
1·1846	37·108	1·0818	16·718
1·1822	36·700	1·0798	16·310
1·1802	36·292	1·0778	15·902
1·1782	35·884	1·0758	15·494
1·1762	35·476	1·0738	15·087
1·1741	35·068	1·0718	14·679
1·1721	34·660	1·0697	14·271
1·1701	34·252	1·0677	13·863
1·1681	33·845	1·0657	13·456
1·1661	33·437	1·0637	13·049
1·1641	33·029	1·0617	12·641
1·1620	32·621	1·0597	12·233
1·1599	32·213	1·0577	11·825
1·1578	31·805	1·0557	11·418
1·1557	31·398	1·0537	11·010
1·1537	30·990	1·0517	10·602
1·1515	30·582	1·0497	10·194
1·1494	30·174	1·0477	9·786
1·1473	29·767	1·0457	9·379
1·1452	29·359	1·0437	8·971
1·1431	28·951	1·0417	8·563
1·1410	28·544	1·0397	8·155
1·1389	28·136	1·0377	7·747
1·1369	27·728	1·0357	7·340
1·1349	27·321	1·0337	6·932
1·1328	26·913	1·0318	6·524
1·1308	26·505	1·0298	6·116
1·1287	26·098	1·0279	5·709
1·1267	25·690	1·0259	5·301
1·1247	25·282	1·0239	4·893
1·1226	24·874	1·0220	4·486
1·1206	24·466	1·0200	4·078
1·1185	24·058	1·0180	3·670
1·1164	23·650	1·0160	3·262
1·1143	23·242	1·0140	2·854
1·1123	22·834	1·0120	2·447
1·1102	22·426	1·0100	2·039
1·1082	22·019	1·0080	1·631
1·1061	21·611	1·0060	1·124
1·1041	21·203	1·0040	0·816
1·1020	20·796	1·0020	0·408

TABLE III.

Specific gravity of dilute Nitric Acid containing different proportions of anhydrous acid, by *Ure.* Temperature 15° C. (59° F.)

Specific gravity.	Per-cents of acid.	Specific gravity.	Per-cents of acid.	Specific gravity.	Per-cents of acid.	Specific gravity.	Per-cents of acid.
1·500	79·7	1·419	59·8	1·295	39·8	1·140	19·9
1·498	78·9	1·415	59·0	1·289	39·0	1·134	19·1
1·496	78·1	1·411	58·2	1·283	38·3	1·129	18·3
1·494	77·3	1·406	57·4	1·276	37·5	1·123	17·5
1·491	76·5	1·402	56·6	1·270	36·7	1·117	16·7
1·488	75·7	1·398	55·8	1·264	35·9	1·111	15·9
1·485	74·9	1·394	55·0	1·258	35·1	1·105	15·1
1·482	74·1	1·388	54·2	1·252	34·3	1·099	14·3
1·479	73·3	1·383	53·4	1·246	33·5	1·093	13·5
1·476	72·5	1·378	52·6	1·240	32·7	1·088	12·7
1·473	71·7	1·373	51·8	1·234	31·9	1·082	11·9
1·470	70·9	1·368	51·1	1·228	31·1	1·076	11·2
1·467	70·1	1·363	50·2	1·221	30·3	1·071	10·4
1·464	69·3	1·358	49·4	1·215	29·5	1·065	9·6
1·460	68·5	1·353	48·6	1·208	28·7	1·059	8·8
1·457	67·7	1·348	47·9	1·202	27·9	1·054	8·0
1·453	66·9	1·343	47·0	1·196	27·1	1·048	7·2
1·450	66·1	1·338	46·2	1·189	26·3	1·043	6·4
1·446	65·3	1·332	45·4	1·183	25·5	1·037	5·6
1·442	64·5	1·327	44·6	1·177	24·7	1·032	4·8
1·439	63·8	1·322	43·8	1·171	23·9	1·027	4·0
1·435	63·0	1·316	43·0	1·165	23·1	1·021	3·2
1·431	62·2	1·311	42·2	1·159	22·3	1·016	2·4
1·427	61·4	1·306	41·4	1·153	21·5	1·011	1·6
1·423	60·6	1·300	40·4	1·146	20·7	1·005	0·8

TABLE IV.

Specific gravity of dilute Acetic Acid containing different proportions of hydrated acid, by *Mohr.*

Per cents.	Specific gravity.	Per cents.	Specific gravity.	Per cents.	Specific gravity.	Per cents.	Specific gravity.	Per cents.	Specific gravity.
100	1·0635	80	1·0735	60	1·067	40	1·051	20	1·027
99	1·0655	79	1·0735	59	1·066	39	1·050	19	1·026
98	1·0670	78	1·0732	58	1·066	38	1·049	18	1·025
97	1·0680	77	1·0732	57	1·065	37	1·048	17	1·024
96	1·0690	76	1·0730	56	1·064	36	1·047	16	1·023
95	1·0700	75	1·0720	55	1·064	35	1·046	15	1·022
94	1·0706	74	1·0720	54	1·063	34	1·045	14	1·020
93	1·0708	73	1·0720	53	1·063	33	1·044	13	1·018
92	1·0716	72	1·0710	52	1·062	32	1·042	12	1·017
91	1·0721	71	1·0710	51	1·061	31	1·041	11	1·016
90	1·0730	70	1·0700	50	1·060	30	1·040	10	1·015
89	1·0730	69	1·0700	49	1·059	29	1·039	9	1·013
88	1·0730	68	1·0700	48	1·058	28	1·038	8	1·012
87	1·0730	67	1·0690	47	1·056	27	1·036	7	1·010
86	1·0730	66	1·0690	46	1·055	26	1·035	6	1·008
85	1·0730	65	1·0680	45	1·055	25	1·034	5	1·007
84	1·0730	64	1·0680	44	1·054	24	1·033	4	1·005
83	1·0730	63	1·0680	43	1·053	23	1·032	3	1·004
82	1·0730	62	1·0670	42	1·052	22	1·031	2	1·002
81	1·0732	61	1·0670	41	1·051	21	1·029	1	1·001

In all cases in which the determination of the specific gravity fails to attain the end in view, or which demand particular accuracy, one of the two following methods is employed, but more commonly the first.

B. DETERMINATION OF THE ANHYDROUS ACID BY SATURATION WITH AN ALKALINE FLUID OF KNOWN STRENGTH.*

§ 215.

This method requires :—

α. A dilute acid of known strength.

β. An alkaline fluid also of known strength.

aa. Preparation of the Solutions.

α. The dilute *acid* must contain in 1000 c.c. the exact equivalent number of the acid ($H = 1$) in grammes, accordingly, 40 grammes of sulphuric acid, 36·46 of hydrochloric acid, 36 of oxalic acid, &c. Acids of this degree of dilution are called *normal* or *standard acids*; equal volumes of them severally neutralize equal quantities of alkalies. The normal or standard sulphuric acid is generally used; or the normal or standard oxalic acid, as recommended by *Mohr*, may be employed.

Preparation of Standard Sulphuric Acid.

Mix, in a large flask, 1020 cubic centimetres of water intimately with 60 grammes of concentrated sulphuric acid; allow the mixture to cool, take two portions of it of 20 c.c. each, and determine the amount of sulphuric acid in them by precipitation with chloride of barium (§ 132. I., 1). If the two experiments agree pretty nearly, take the mean of the results as the amount of sulphuric acid contained in the solution, and dilute the latter with the necessary quantity of water to give a fluid *containing in* 1000 *c.c. exactly* 40 *grammes* of anhydrous sulphuric acid. Suppose that 1000 c.c. of the solution contain 42 grammes of sulphuric acid, then, according to the proportion,

$$40 : 1000 :: 42 : x;\ x = 1050,$$

you will have to add 50 c.c. of water to 1000 c.c. of the solution. This may be effected most simply and accurately in the following manner :—

Fill a measuring flask holding 1 litre, up to the litre mark with the dilute acid, and pour the latter from this flask cautiously into a larger bottle; measure in a pipette 50 c.c. of water, transfer to the measuring flask which contained the acid, shake the water well about in the flask, and then add it to the solution in the larger bottle. Shake the mixture well, pour back about half into the measuring flask, shake about in the latter, and then transfer again to the large bottle. Shake, and keep for use. As the fluid only half fills the larger bottle, water will after a time evaporate, which will condense on the sides in the upper part of the vessel; it is necessary, therefore, to shake the bottle each time before using its contents; otherwise the portion poured out first will contain more water, and accordingly less acid, than the remaining fluid.

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* According to *Nicholson* and *Price* ("Chem. Gaz.," 1856, p. 30) the common method of acidimetry is not suited for determining free acetic acid, on account of the alkaline reaction of neutral acetate of soda; however, *Otto* ("Annal. d. Chem. u. Pharm.," 102, 69) has clearly demonstrated that the error arising from this is so inconsiderable that it may safely be disregarded.

Preparation of Standard Oxalic Acid.

Introduce 1 equivalent, *i.e.*, 63 grammes, of pure crystallized oxalic acid (C_2O_3, $HO + 2\,Aq$), accurately weighed, into a litre flask, add water at 60° F., dissolve by shaking, dilute up to the litre mark with water at 60° F., shake, and keep for use. The solution must be shaken each time previous to using it, for the same reason as the sulphuric acid solution. Care must be taken to employ perfectly pure oxalic acid, absolutely free from moisture, and without the least sign of efflorescence.

β. For *alkaline solution* a solution of soda is used, of which 1 *volume exactly neutralizes* 1 *volume of standard acid;* the point of neutralization being indicated by the blue coloration imparted by the last drop of solution of soda added to the acid solution slightly reddened by litmus. An alkaline solution of this strength is called *normal or standard solution of soda.* 1000 c.c. of it saturate 1 equivalent of each acid ($H = 1$), expressed in grammes.

To effect this, dilute a fresh prepared, perfectly clear solution of soda, quite free from carbonic acid, to a specific gravity of about 1·05, which corresponds to about 3·6 per cent. of soda. Measure off 50 c.c. of the standard acid, transfer to a beaker, impart a faint red tint to the fluid by means of tincture of litmus,* and let the standard solution of soda flow into the reddened fluid, from a burette with compression-clamp, until the mixture just shows a blue tint, and consequently leaves both red and blue litmus paper unaltered. Dilute now the still somewhat too concentrated solution of soda with the requisite quantity of water to give a fluid of which exactly 50 c.c. are required to saturate 50 c.c. of the standard acid. Suppose, therefore, you have used 47 c.c. of the solution of soda, you will have to add 3 c.c. of water to every 47 c.c. of the solution, and accordingly 63·83 c.c. of water to 1 litre. The best way of effecting this dilution has already been described in *α*. Close the flask in which the dilute solution of soda is kept, with a cork into which is fitted a small bulb tube of the form of a chloride of calcium tube, filled with a finely triturated mixture of sulphate of soda and caustic lime, and bearing a thin open tube in the exit aperture (*Mohr*). Besides this solution of soda, prepare another, 5 times more dilute, and a third, 10 times more dilute. This is effected best—for instance, as regards the latter fluid—by measuring in a pipette 50 c.c. of the more concentrated solution of soda, transferring the fluid to a measuring flask holding exactly 500 c.c., then filling the flask with water, exactly up to the mark, and mixing intimately by shaking.

bb. The Volumetrical Process.

As 1000 c.c. of the standard solution of soda correspond to 1 equivalent, 1000 c.c. of the 5 times more dilute solution to $\frac{1}{5}$, and 1000 c.c. of the decimal solution to $\frac{1}{10}$ equivalent of each acid expressed in grammes, there is hardly anything further to be said about the process, the selection of either of the three alkaline fluids depending, of course, entirely upon the quantity of acid to be neutralized. The neutralization of the weighed or measured acid fluid should take about 15—30 c.c.

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* As the tincture of litmus is often so alkaline that a notable amount of acid is required to redden it, the excess of alkali must, if necessary, be neutralized; the tincture so prepared gives upon dilution with water a violet-colored fluid, to which a trace of acid imparts a red, and the least quantity of alkali a blue tint (§ 65, 2).

In scientific investigations, I recommend the weighing of indeterminate quantities of the acid fluid, as this may be done with comparative ease on a chemical balance, and the trifling trouble of calculation is not worth mentioning. Suppose, for instance, you have weighed off 4·5 grms. of dilute acetic acid, and used 25 c.c of standard solution of soda to neutralize this, you find by the proportion,

$$1000 : 60 \text{ (equivalent of } C_4H_4O_4) :: 25 : x$$
$$x = 1\cdot5,$$

that 1·5 grms. of hydrated acetic acid are contained in the weighed quantity of the dilute acid; and another proportion, viz.,

$$4\cdot5 : 1\cdot5 :: 100 : x;\ x = 33\cdot\dot{3}\dot{3},$$

gives the per-centage amount of hydrated acetic acid contained in the analysed fluid. Or, the calculation may also be made as follows:—

4·5 grms. of the acetic acid examined having required 25 c.c. of standard solution of soda for neutralization, how much would 6 grammes (*i.e.* the weight of $\frac{1}{10}$ equivalent of hydrated acetic acid) require?

$$4\cdot5 : 25 :: 6 : x;\ x = 33\cdot\dot{3}\dot{3}$$

It is evident that in this case the number of cubic centimetres found as x, expresses the per-centage amount of hydrated acetic acid contained in the examined fluid, since 100 c.c. of standard solution of soda correspond to $\frac{1}{10}$ equivalent of pure hydrated acetic acid, *i.e.* acetic acid of 100 per cent.

In technical analyses it is more convenient if the number of c.c., or half c.c. used of the standard solution of soda expresses directly, and without need of further calculation, the per-centage amount of hydrated or anhydrous acid contained in the examined fluid. For this purpose, the $\frac{1}{10}$ or $\frac{1}{20}$ equivalents (H = I) of the anhydrous or hydrated acid, expressed in grammes, are weighed off—the $\frac{1}{10}$ equivalents if the number of c.c., the $\frac{1}{20}$ equivalents if the number of half c.c. used of standard solution of soda, are to express the per-centage amount of hydrated or anhydrous acid contained in the analysed fluid.

The following are the quantities for the more common acids:—

	$\frac{1}{10}$ Equivalent in gramm[illegible]	$\frac{1}{20}$ Equivalent in grammes.
Sulphuric acid	4·0	2·00
Hydrated sulphuric acid	4·9	2·45
Nitric acid	5·4	2·70
Hydrated nitric acid	6·3	3·15
Hydrochloric acid	3·646	1·823
Oxalic acid	3 6	1·80
Crystallized oxalic acid	6·3	3·15
Acetic acid	5·1	2·55
Hydrated acetic acid	6·0	3·00
Tartaric acid	6·6	3·30
Hydrated tartaric acid	7·5	3·75

But, as the weighing of definite small quantities is less accurate, it is preferable to weigh off the half equivalents of the acids (*i.e.* 20 or 24·5 grammes of sulphuric acid, according to whether it is intended to find the per-centage amount of anhydrous or of hydrated acid; 18·23 of hydrochloric acid, &c.) in a measuring flask holding 500 c.c., add water cautiously,* allow to cool if necessary, fill up with water to the mark, shake, and then remove, by means of the pipette, 100 or 50 c.c., according to whether $\frac{1}{10}$ or $\frac{1}{20}$ equivalent of acid is to be used.

Chemists occasionally prefer using solution of soda of tolerably correct concentration, the strength of which has been determined by saturating with it accurately measured quantities of standard sulphuric or standard oxalic acid. This renders a little rule-of-three calculation indispensable. Suppose 18·5 of solution of soda are found to correspond to 10 c.c. of standard sulphuric acid, *i.e.* $\frac{1}{100}$ equivalent = 0·4 grm. of sulphuric acid, they will correspond equally to the $\frac{1}{100}$ equivalents of all other acids, accordingly, for instance, to 0·6 grm. of hydrated acetic acid. Now, supposing 12 grammes of the solution of soda to have been used to saturate 10 grms. of vinegar, the per-centage amount of hydrated acetic acid contained in the latter will be found by the following proportion :—

$$18{\cdot}5 : 0{\cdot}6 :: 12 : x;\ x = 0{\cdot}389,$$

and expressed in per-cents.,

$$10 : 0{\cdot}389 :: 100 : x;\ x = 3{\cdot}89$$

The acidimetric principle may often be employed also for the determination of acids in combination with bases, if solution of soda precipitates the latter completely, and in a state of absolute purity. For instance, acetic acid in iron liquor, or in verdigris, may be estimated in this way, by the following process :—Precipitate with a measured quantity of standard solution of soda in excess, boil, filter, wash, concentrate the filtrate, add standard acid to acid reaction; boil, to expel the carbonic acid, which the soda solution may have absorbed in the process of evaporation, redden with litmus, and add solution of soda until a blue tint is imparted to the fluid. Subtract the amount of standard acid used from the total quantity of soda solution consumed in the experiment; the difference expresses the quantity of soda solution neutralized by the acid contained in the examined substance, in combination as well as in the free state. Of course, reliable results can be expected only if no basic salt has been thrown down by the soda solution.

MODIFICATION OF THE COMMON ACIDIMETRIC METHOD (recommended by *Kiefer*, "Annal. d. Chem. u. Pharm.," 93, 386).

§ 216.

Instead of estimating the free acid by a solution of soda of known strength, and determining the neutralization point by means of litmus solution, an ammoniacal solution of oxide of copper may be used for the purpose, in which case the neutralization point is known by the turbidity observed as soon as the free acid present is completely neutralized. The copper solution is prepared by adding to an aqueous solution of sulphate of copper, solution of ammonia until the precipitate of basic salt which forms at first is just redissolved. After determining the strength of the solution by standard sulphuric acid (not standard oxalic acid), it may be employed for the estimation of all stronger acids (with the exception of oxalic acid), provided the fluids are clear. Dilution does not alter the reaction, and the terminal point of it may be recognised with sufficient accuracy. This method is of especial value in cases in which free acid is to be determined in presence of a neutral metallic salt with acid reaction—*e.g.*, free sulphuric acid in mother-liquors of sulphate of copper or sulphate of zinc, &c. It is advisable to determine the strength of the ammoniacal copper solution anew before every fresh experiment.

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* Concentrated sulphuric acid must be weighed into the properly tared flask, already half filled with water.

C. ESTIMATION BY WEIGHING THE CARBONIC ACID EXPELLED BY THE FREE ACID FROM BICARBONATE OF SODA (*Fresenius* and *Will*).

§ 217.

Weigh a portion of the acid under examination in the flask A (Fig. 139), and if the acid is concentrated, add water; the fluid should occupy about $\frac{1}{3}$ of the flask. Fill a small glass tube compactly with bicarbonate of soda or potassa,* tie a thread round it, and suspend it by this in the flask A, by confining the thread between the cork and the neck of the flask; arrange the apparatus exactly in the manner described in § 139, II., *e*, *a*, *aa*, and equipoise it on the balance. Release the thread, by raising the cork, whereupon the small tube, together with the thread, will drop into the flask A; insert the cork again air-tight the instant the thread is released. A lively evolution of carbonic acid commences at once, which continues for some time at a uniform rate, then diminishes, and ultimately ceases altogether. When this point is reached, put the flask A in a water-bath of about 122—131° F. When the renewed evolution of carbonic acid to which this proceeding has given rise, has again ceased, open the wax stopper, *b*, on the tube, *a*, a little, remove the flask from the water-bath, and apply suction to *d*, by means of a perforated cork, or India-rubber tube, until all the carbonic acid still lingering in the apparatus is replaced by atmospheric air. Let the apparatus cool; replace it now on the balance and put additional weights on the other scale until the equilibrium is restored. The weight added gives the quantity of carbonic acid expelled. For each equivalent of acid used, 2 equivalents of carbonic acid are obtained; *e.g.* ($\mathrm{Na\,O, 2\,C\,O_2 + N\,O_5 = Na\,O, N\,O_5 + 2\,C\,O_2}$). The results are very satisfactory. In this method also all calculation may be avoided, by weighing off the exact quantity of acid which, if it were pure and anhydrous, would be required to give 1 gramme of carbonic acid; the number of centigrammes of carbonic acid obtained indicates in that case directly the per-centage amount of anhydrous acid contained

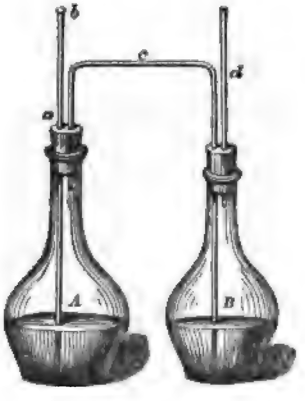

Fig. 139.

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* The bicarbonate used may contain chloride of sodium, sulphate, &c.; but it must be quite free from neutral carbonate; the quantity must be more than sufficient to saturate the acid in the flask.

in the examined fluid. The quantity required is found for sulphuric acid, for instance, by the following proportion :—

$$44 : 40 :: 1{\cdot}00 : x ;\ x = 0{\cdot}909.$$

Instead of the quantities based upon the production of 1 gramme of carbonic acid, multiples of them may of course be employed, according as the degree of dilution of the acid under examination may require. But in that case the number of centigrammes of carbonic acid obtained must be divided by the number corresponding to the multiple ; the quotient gives the per-centage amount of anhydrous acid contained in the examined fluid. The best way is always to take a sufficient quantity of the acid to give from 1 to 2 grammes of carbonic acid.

This method deserves the preference over Method B only in the case of colored fluids, in which the litmus reaction cannot be distinctly observed.

2. Estimation of the Amount of free Alkali and Alkaline Carbonate contained in a Substance (Alkalimetry).

A. Estimation of Potassa, Soda, or Ammonia, from the Specific Gravity of their Solutions.

§ 218.

In pure or nearly pure solutions of hydrated soda or potassa, or of ammonia, the per-centage amount of alkali may be estimated from the specific gravity of the solution.

TABLE I.

Per-centage amounts of Anhydrous Potassa corresponding to different specific gravities of solution of potassa.

Dalton.		*Tünnermann* (at 59° F.).			
Spec. grav.	Per-centage amounts of anhydrous potassa.	Spec. grav.	Per-centage amounts of anhydrous potassa.	Spec. grav.	Per-centage amounts of anhydrous potassa.
2·40	39·9	1·3300	28·290	1·1437	14·145
2·20	36·8	1·3131	27·158	1·1308	13·013
1·42	34·4	1·2966	26·027	1·1182	11·882
1·39	32·4	1·2803	24·895	1·1059	10·750
1·36	29·4	1·2648	23·764	1·0938	9·619
1·83	26·3	1·2493	22·632	1·0819	8·487
1·28	23·4	1·2342	21·500	1·0703	7·355
1·23	19·5	1·2268	20·935	1·0589	6·224
1·19	16·2	1·2122	19·803	1·0478	5·002
1·15	13·0	1·1979	18·671	1·0369	3·961
1·11	9·5	1·1839	17·540	1·0260	2·829
1·06	4·7	1·1702	16·408	1·0153	1·697
		1·1568	15·277	1·0050	0·5658

TABLE II.

Per-centage amounts of Anhydrous Soda corresponding to different specific gravities of solution of soda.

Dalton.		*Tünnermann* (at 59° F.).					
Specific grav.	Per-centage amount of anhydrous soda.	Spec. grav.	Per-centage amounts of anhydrous soda.	Spec. grav.	Per-centage amounts of anhydrous soda.	Spec. grav.	Per-centage amounts of anhydrous soda.
2·00	77·8	1·4285	30·220	1·2982	20·550	1·1528	10·275
1·85	63·6	1·4193	29·616	1·2912	19·945	1·1428	9·670
1·72	53·8	1·4101	29·011	1·2843	19·341	1·1330	9·066
1·63	46·6	1·4011	28·407	1·2775	18·730	1·1233	8·462
1·56	41·2	1·3923	27·802	1·2708	18·132	1·1137	7·857
1·50	36·8	1·3836	27·200	1·2642	17·528	1·1042	7·253
1·47	34·0	1·3751	26·594	1·2578	16·923	1·0948	6·648
1·44	31·0	1·3668	25·989	1·2515	16·319	1·0855	6·044
1·40	29·0	1·3586	25·385	1·2453	15·714	1·0764	5·440
1·36	26·0	1·3505	24·780	1·2392	15·110	1·0675	4·835
1·32	23·0	1·3426	24·176	1·2280	14·506	1·0587	4·231
1·29	19·0	1·3349	23·572	1·2178	13·901	1·0500	3·626
1·23	16·0	1·3273	22·967	1·2058	13·297	1·0414	3·022
1·18	13·0	1·3198	22·363	1·1948	12·692	1·0330	2·418
1·12	9·0	1·3143	21·894	1·1841	12·088	1·0246	1·813
1·06	4·7	1·3125	21·758	1·1734	11·484	1·0163	1·209
		1·3053	21·154	1·1630	10·879	1·0081	0·604

TABLE III.

Per-centage amounts of Ammonia (NH_3) corresponding to different specific gravities of solution of ammonia at 16° C. = 60·8° F. (*J. Otto*).

Spec. grav.	Per-centage amounts of ammonia.	Spec. grav.	Per-centage amounts of ammonia.	Spec. grav.	Per-centage amounts of ammonia.
0·9517	12·000	0·9607	9·625	0·9697	7·250
0·9521	11·875	0·9612	9·500	0·9702	7·125
0·9526	11·750	0·9616	9·375	0·9707	7·000
0·9531	11·625	0·9621	9·250	0·9711	6·875
0·9536	11·500	0·9626	9·125	0·9716	6·750
0·9540	11·375	0·9631	9·000	0·9721	6·625
0·9545	11·250	0·9636	8·875	0·9726	6·500
0·9550	11·125	0·9641	8·750	0·9730	6·375
0·9555	11·000	0·9645	8·625	0·9735	6·250
0·9556	10·950	0·9650	8·500	0·9740	6.125
0·9559	10·875	0·9654	8·375	0·9745	6·000
0·9564	10·750	0·9659	8·250	0·9749	5·875
0·9569	10·625	0·9664	8·125	0·9754	5·750
0·9574	10·500	0·9669	8·000	0·9759	5·625
0·9578	10·375	0·9673	7·875	0·9764	5·500
0·9583	10·250	0·9678	7·750	0·9768	5·375
0·9588	10·125	0·9683	7·625	0·9773	5·250
0·9593	10·000	0·9688	7·500	0·9778	5·125
0·9597	9·875	0·9692	7·375	0·9783	5·000
0·9602	9·750				

B. ESTIMATION OF THE TOTAL AMOUNT OF CAUSTIC ALKALI AND ALKALINE CARBONATE IN SODA AND POTASH OF COMMERCE.

It is well known that the potash and soda of commerce consist of a mixture of alkaline carbonate with a number of other salts. The commercial value of potash and soda depends entirely upon the proportional amount of alkaline carbonate (or caustic alkali) in them, the admixed salts being of no value to the purchaser. Now, as the quantity of the latter is very variable, it is evident that the commercial value of a sample of soda or potash submitted to the analysist can be determined only by ascertaining the proportion of alkaline carbonate (or caustic alkali) contained in it.

I will give here two methods of alkalimetry, based upon essentially different principles, viz., a volumetric method, and a gravimetric method. The former, being more expeditious, is most commonly employed; the latter, however, gives more accurate results. As will be seen in § 222, both methods are occasionally combined, in cases where it is wished to determine separately both the quantities of alkaline carbonate and caustic alkali.

I. *Alkalimetric Method of Descroizilles and Gay-Lussac, slightly modified.*

§ 219.

The principle of this method is the same as that on which the acidimetrical method described § 215, is based, *i.e.* if we know the quantity of an acid of known strength, required to saturate an unknown quantity of caustic potassa or soda, or of carbonate of potassa or soda, we may readily calculate from this the amount of alkali present.

The process requires only *one* fluid of known strength, viz., a standard sulphuric acid.

This is now almost universally made of that exact strength that 50 c.c. saturate 5 grammes of pure anhydrous carbonate of soda.

The following is the most simple way of preparing it:

a. Mix about 60 grammes of concentrated sulphuric acid with 500 c.c., or 120 grammes with 1000 c.c. of water, and let the mixture cool.

b. Weigh off accurately 5 grammes of pure anhydrous carbonate of soda, transfer to a flask, dissolve in about 200 c.c. of water, and color the solution blue with a measured quantity (1 or 2 c.c.) of violet tincture of litmus (see § 215, *aa*, *β*, foot-note).

> N.B. This instruction is addressed only to those who do not weigh on delicate balances. Where chemical balances are used, as in laboratories, it answers the purpose much better to ignite gently in a platinum crucible between 4·5 and 5 grammes of carbonate of soda, let the crucible cool under the exsiccator, and then weigh it accurately with its contents. Transfer the latter to the flask, and weigh the crucible; in this manner the exact quantity of carbonate of soda in the flask is most accurately ascertained. An experienced chemist, accustomed to the use of a delicate balance, performs this process with greater facility and expedition than the other; the results are also far more reliable, as the substance is weighed in a covered crucible. The potassa or soda to be examined is afterwards weighed in the same manner as the pure carbonate of soda.

c. Fill the burette up to the 0 mark with the cold dilute acid, and allow it to flow into the solution of soda, until complete saturation is effected (see below). This experiment should be made twice. If the quantity of carbonate of soda was not exactly 5 grammes, calculate from the results obtained how much acid the saturation of 5 grammes would have required.

d. Dilute the acid remaining with a sufficient quantity of water to give a standard fluid, of which exactly 50 c.c. are required to saturate 5 grammes of carbonate of soda. Suppose it has taken in the experiments (*c*) 40 c.c. of the acid to saturate 5 grammes of carbonate of soda, 10 volumes of water must be added to 40 volumes of the acid. This dilution of the acid is effected best in the manner described § 215, *aa*. Test the dilute acid now once more as above described. Keep the standard acid in well-stoppered bottles, and shake before every new series of experiments (see § 215, *aa*, *α*). This standard acid serves for the examination of all alkaline fluids; it indicates directly the percentage amount of alkaline carbonate or caustic alkali present, provided the experiment is made with a weighed quantity of the alkaline fluid equivalent to 5 grammes of carbonate of soda.

The following table shows the equivalent quantities:—

50 c.c. of the standard acid	saturate	5·000	grammes of	carbonate of soda.
„	„	2·925	„	soda.
„	„	6·519	„	carbonate of potassa.
„	„	4·443	„	potassa.

Accordingly, if we take 6·519 grammes of a sample of potassa, the number of half c.c. used of the standard acid gives directly the per-centage amount of alkali, expressed as carbonate of potassa; if 4·443 grammes are taken, the number of half c.c. used of the standard acid gives the percentage amount of alkali, expressed as anhydrous caustic potassa, &c.

In the examination of substances poor in alkaline carbonates or in caustic alkalies, a multiple (the double, triple, &c) of the quantities given above is used, the number of half c.c. required of the standard acid being afterwards divided by the corresponding number (2, 3, &c.).

With respect to the process, we have to consider the following additional points:—

1. *Determination of the point of saturation.*

With caustic alkalies it is easy to neutralize exactly; but in the case of alkaline carbonates, the liberated carbonic acid, which imparts a wine-red color to the fluid, causes some difficulty. This may be overcome in two different ways.

a. When you have added to the cold, or, as the case may be, already previously heated, solution of soda or potassa, sufficient of the standard acid to impart a wine-red color to the fluid, heat to ebullition, with frequent shaking: in proportion as the carbonic acid escapes, the fluid will change from red to blue. If some more standard acid is now added to the nearly boiling fluid, the vessel being occasionally replaced on the lamp, it is easy to hit the exact point of saturation, or, more correctly speaking, of beginning supersaturation, which is indicated by the red color of the fluid, slightly inclining to yellow.

b. The point of saturation may be attained, also, though not with the same degree of accuracy, without applying heat. A rather capacious flask is indispensable in this experiment. After every fresh addition of standard acid, the fluid is carefully and vigorously shaken. The addition of the standard acid may be continued as long as the red color of the fluid continues to show a tint of violet. When the point of saturation is at last approaching, the acid is added more cautiously, two drops at a time ; after every fresh addition, a glass rod is dipped into the fluid, and one or, better, two spots made with it on a slip of fine blue litmus paper, the volume being read off each time, and the number marked between the spots. The operation is continued in this way until the spots on the litmus paper appear positively red. The paper is then allowed to dry, and *that* lowest number is taken for the correct one where the spots between which it is marked just remain red.

Let it be borne in mind, as a rule, that the standard acid must be tested by the same method which it is intended to use subsequently in the process. For this reason a standard sulphuric or oxalic acid, as prepared according to the directions of § 215, cannot be employed for the direct and immediate estimation of the alkali in soda and potash of commerce.

2. *With regard to the examination of potash by this method,* the following points deserve attention :—

The various sorts of potash of commerce contain, besides carbonate of potassa,

a. Neutral salts (*e. g.*, sulphate of potassa, chloride of potassium).

b. Salts with alkaline reaction (*e. g.*, silicate of potassa, phosphate of potassa).

c. Admixtures insoluble in water, more especially carbonate, phosphate, and silicate of lime.

The salts named in *a* exercise no influence upon the results, but not so those named in *b* and *c*. Those in *c* may be removed by filtration ; but the admixture of the salts named in *b* constitutes an irremediable, though slight source of error.

If it is required to ascertain whether a sample of potash contains, besides the other salts mixed with the carbonate of potassa, also water, the determination of the latter substance must precede the alkalimetrical examination (§ 221, *a*). The same remark applies also to soda.

3. With regard to *the examination of soda by this method,* the following points deserve attention :—

The soda of commerce, prepared by *Leblanc's* method, contains, besides carbonate of soda, always, or at least generally, hydrate of soda, sulphate of soda, chloride of sodium, silicate and aluminate of soda, and not seldom also sulphide of sodium, hyposulphite and sulphite of soda.*

The presence of the three last-named substances and of the silicate d aluminate of soda, impedes the process, and interferes more or less with the accuracy of the results. The presence of the silicate and aluminate of soda is usually indicated by the precipitate which the solution of soda deposits when saturated with acid ; that of the other three substances is ascertained in the following way :—

a. Mix with sulphuric acid ; a smell of sulphuretted hydrogen reveals the presence of *sulphide of sodium,* with which hyposulphite of soda is also invariably associated.

b. Color dilute sulphuric acid with a drop of solution of permanganate of potassa or chromate of potassa, and add some of the soda under examination, but not sufficient to neutralize the acid. If the solution retains its red or reddish-yellow color, this proves the absence of both sulphite and hyposulphite of soda; but if the fluid loses its color, or turns green, one of these salts is present.

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* Traces of cyanide of sodium are also occasionally found.

c. Whether the reaction described in *b* proceeds from sulphite or hyposulphite of soda, is ascertained by supersaturating a clear solution of the sample under examination with hydrochloric acid. If the solution, after the lapse of some time, becomes turbid, owing to the separation of sulphur (emitting at the same time the odor of sulphurous acid), this may be regarded as a proof of the presence of hyposulphite of soda; however, the solution may, besides the hyposulphite, also contain sulphite of soda.

The defects arising from the presence of the three last-named compounds may be remedied in a measure, by igniting the weighed sample of the soda with chlorate of potassa, before proceeding to saturate it. This operation converts the sulphide of sodium, hyposulphite of soda, and sulphite of soda, into sulphate of soda. But if hyposulphite of soda is present, the process serves to introduce another source of error, as that salt, upon its conversion into sulphate of soda, decomposes an equivalent of carbonate of soda, and expels the carbonic acid of the latter [$Na\,O, S_2O_2 + 4\,O$ (proceeding from the chlorate of potassa) $+ Na\,O, CO_2 = 2\,(Na\,O, SO_3) + CO_2$].

§ 220.

Instead of estimating the alkalies in the direct way by means of an acid of known strength, we may estimate them also, as proposed first by *Fr. Mohr* ("Annal. d. Chem. u. Pharm.," 86, 129), by supersaturating with standard acid, expelling the carbonic acid by boiling, and finally determining by solution of soda the excess of standard acid added.

This process gives very good results, and is particularly suited for scientific investigations. It requires the standard fluids mentioned in § 215, viz., standard sulphuric or oxalic acid, and standard solution of soda. Each of these fluids is kept in a separate burette, with caoutchouc connector and compression clamp.

The process is as follows:—

Dissolve the alkali in water, and color the solution slightly blue with a measured quantity of litmus tincture; let now as much of the standard acid flow into it from the burette as will suffice to impart a violet tint to the fluid; then boil, add more acid, until the color is distinctly yellowish red, then a further quantity, to fill up to the next cubic centimetre line. The alkali is now decidedly supersaturated; remove the last traces of carbonic acid, by boiling, shaking, blowing into the flask, and finally sucking out the air.

Now add the standard solution of soda, drop by drop, until the color just appears light blue. If the alkaline fluid is free from carbonic acid, and only slightly colored with litmus tincture, there is no difficulty in determining the exact point at which the reaction is completed; whereas, if the reverse is the case, this point cannot be determined with accuracy, as the blue tint just imparted to the fluid by the solution of soda for some time continues to change again to violet.

If the standard solution of soda and the standard acid used are of corresponding strength, the number of c.c. used of the soda solution is simply deducted from the number of c.c. used of the standard acid. The difference expresses the quantity of acid neutralized by the alkali in the examined sample. If the two standard fluids are not of corresponding strength, the excess of acid added, and subsequently neutralized by the soda solution, is calculated from the known proportion the one bears to the other.

If $\frac{1}{10}$ equivalents (H = 1), in grammes, have been weighed of the alkalies to be valued, of soda accordingly, 5·3 grms., of potash 6·91 grms., the number of c.c. used of the standard acid expresses directly the per-centage amount of carbonate of soda or carbonate of potassa contained in the examined sample; since 100 c.c. of the standard acid, containing $\frac{1}{10}$ eq. of acid will just suffice to neutralize $\frac{1}{10}$ eq. of pure carbonate of soda or carbonate of potassa.* If any other given quantities of the alkalies have been weighed off, a simple calculation will give the per-centage amount of carbonate of soda or carbonate of potassa contained in the examined sample.

To make this simple calculation quite clear for all possible cases, I select the most complicated one, proceeding upon the supposition that the soda solution is not of corresponding strength with the standard acid, but that 2·2 c.c. of the soda solution neutralize 1 c.c. of the standard acid; and that instead of $\frac{1}{10}$ eq., 3·71 grms. of potash have been weighed off.

The quantity of standard acid added was 48 c.c.; the excess required 4·3 c.c. of soda solution for neutralization. The proportion

$$2{\cdot}2 : 1 :: 4{\cdot}3 : x;\ x = 1{\cdot}95$$

shows that the excess of acid was 1·95 c.c.; 48—1·95 = 46·05 c.c. of the acid have accordingly been consumed by the potash. The proportion

$$3.71 : 46{\cdot}05 :: 6{\cdot}91\ (\tfrac{1}{10}\text{ eq. } KO, CO_2) : x;\ x = 85{\cdot}77$$

shows that the examined potash contains 85·77 per cent. of alkaline carbonate.

II. *Fresenius and Will's Method.*

§ 221.

In this method the quantity of alkaline carbonate contained in a sample of potash or soda is calculated from the amount of carbonic acid disengaged from it. Its application demands therefore that all the alkali, which constitutes its commercial value, be present in the form of a neutral carbonate, and that the substance contain no other carbonate besides this. If the sample under examination fails to satisfy these conditions, it must be treated in the proper manner to bring them about.

The determination of the carbonic acid is effected in the way described § 139, II., *e*, *a*, *aa*. The flasks of the apparatus, illustrated in Fig. 66, should not be too small: A should hold from 2 to 2½, B from 1½ to 2 ounces of water. Though not absolutely necessary, it is always advisable to precede the determination of the carbonic acid by a quantitative estimation of the water contained in the sample under examination.

1. *Examination of Potash.*

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* Of 100 per cent

a. Determination of the Water.

Place a small dish of sheet iron, about 2 inches in diameter, and provided with a somewhat loose-fitting cover, on one scale of a balance together with a 10-gramme weight; equipoise the balance accurately by putting on the other scale small shot, and ultimately slips of tin-foil. Take several samples of the potash from different parts of the mass, triturate with the greatest expedition in a dry mortar, remove the 10-gramme weight, and put portions of the pulverized potash into the dish until the equilibrium is perfectly restored.

You have now exactly 10 grammes of the potash in the dish. Apply a gentle heat to the latter, until the whole of the water is expelled, which may be ascertained by holding a glass plate over the open dish, and observing whether any aqueous vapor continues to condense upon it or not. Cover the dish, allow it to cool under the exsiccator, then replace it on the balance, and restore the equilibrium by adding weights. The number of decigrammes required to restore the equilibrium indicates directly the amount of water contained in every 100 parts of the examined potash.

A porcelain crucible with lid may be used instead of the iron dish.

b. Determination of the Carbonic Acid.

Weigh off 6·283 grammes of the anhydrous residue of *a*, and determine the carbonic acid contained in that quantity, as directed § 139, II., *e*, *a*, *aa*. Divide by 2 the number of centigrammes of carbonic acid disengaged: the result expresses the quantity of carbonate of potassa contained in the examined sample. Suppose 6·283 grammes of potash have given 1·80 grm. of carbonic acid (indicated by the loss of weight of the apparatus), the examined sample contains $\frac{180}{2} = 90$ per cent. of carbonate of potassa. If you prefer weighing off, instead of 6·283 grms., any other quantity of potash, you have to calculate subsequently from the results obtained how much carbonic acid 6·283 grms. of potash would have given.

If the potash contains carbonate of lime, which, however, is only very rarely the case, dissolve in water, filter, concentrate the filtrate by evaporation, and then proceed in the manner just now directed (*b*). In presence of sulphide of potassium and caustic potassa, proceed as with soda under the same circumstances (see 2).

2. *Examination of Soda.*

The general method is the same as in 1; 4·817 grammes of the anhydrous residue are weighed off instead of 6·283 grammes. The number of centigrammes of carbonic acid disengaged is divided by 2.

If a soda contains sulphide of sodium, sulphite, or hyposulphite of soda, the liberation of the carbonic acid by the common process would be attended with the disengagement of sulphuretted hydrogen or sulphurous acid, which would of course go to swell the apparent amount of the carbonic acid. This defect may be readily remedied by adding to the solution of soda in A, a small quantity of solution of neutral chromate of potassa, which will effect the decomposition of the sulphuretted hydrogen or sulphurous acid; and the products of this decomposition being non-volatile, the carbonic acid only will be evolved. As most sorts of soda of commerce contain admixtures of either the one or the other of the substances named, and as it is far more simple to add at once some chromate of potassa to the soda solution than to test the latter first for the presence of either of the three salts—it is always advisable to make it a rule, in the examination of soda, to add some chromate of potassa.

If the soda under examination contains a very large proportion of chloride of sodium, addition of a considerable excess of sulphuric acid must be carefully avoided, as otherwise a perceptible amount of hydrochloric acid, and, in presence of an alkaline chromate, with application of a stronger heat, chlorine also will escape. The heating of the fluid still containing absorbed carbonic acid, which is required at the end of the process, should therefore be effected by means of a small sand-bath, and not in the usual way, *i.e.*, by the addition of more sulphuric acid.

If the soda under examination contains caustic soda, which may be detected by the alkaline reaction manifested by the solution of the sample after addition of chloride of barium in excess, the following modification of the common method is adopted.

a. DETERMINATION OF THE WATER.

This is effected in the usual way (see 1, *a*, Examination of Potash).

b. DETERMINATION OF THE CARBONIC ACID.

Weigh off 4·817 grammes of the anhydrous residue of *a*, and triturate in a mortar with 3 or 4 parts of pure quartz sand, and about $\frac{1}{5}$ of carbonate of ammonia in powder; transfer the mixture to a small iron dish, and rinse the mortar with sand, transferring the sand used also to the dish. Moisten the mass in the dish with as much water as it can absorb; let it stand a short time, and then heat gently until the water is completely expelled. The residue now no longer contains the least trace of carbonate of ammonia. If the soda under examination contains sulphide of sodium besides caustic soda, the mass in the dish is moistened with solution of caustic ammonia instead of water, to effect the reduction of the sesqui-carbonate of ammonia to neutral carbonate; otherwise sulphide of ammonium would be formed, and part of the sulphide of sodium converted into carbonate of soda.

When the mass is cold, transfer it from the dish to the flask A (which may be readily effected with the aid of a spatula); rinse the dish with a little water, and pour this also into A. Conduct the rest of the process in the usual way. The addition of sand is intended to prevent the caking of the mass, and the spurting which would otherwise attend the expulsion of the water, unless the greatest caution were used in the process of heating; moreover, the perfect removal of the dried mass from the dish would be rather difficult but for the sand.

The latter operation (viz., the transfer of the mass from the dish to the flask) may be still more facilitated by coating the inside of the dish with fine sand previously to the introduction of the mixture; this is effected most simply by moistening the inner sides and bottom of the dish with water, throwing a handful of fine sand into it, and shaking out the superfluous quantity.

§ 222.

There now still remain two questions to be considered, which are of importance for the estimation of the commercial value of potash and soda. The first concerns the separate determination of the caustic alkali, which the sample under examination may contain besides the carbonate; the second, the determination of carbonate of soda in presence of carbonate of potassa.

C. DETERMINATION OF THE CAUSTIC ALKALI WHICH COMMERCIAL POTASH AND SODA MAY CONTAIN BESIDE THE CARBONATE.

Many kinds of potash and soda, more especially the latter, contain, besides alkaline carbonate, also caustic alkali; and the chemist is often called upon to determine the amount of the latter; as it is, for instance, by no means a matter of indifference to the soap-boiler how much of the soda is supplied to him already in the caustic state. This may be effected most simply by combining the method described in § 219 or in § 220 with the one given in § 221, *i.e.*, determining by one of the former the total amount of caustic and carbonated alkali expressed in per-cents of carbonate of soda or carbonate of potassa, and estimating by the latter—of course without previous treatment with carbonate of ammonia—the quantity of carbonic acid, and therefore also of alkaline carbonate. The difference between the result of the two processes indicates accordingly the quantity of alkaline carbonate corresponding to the caustic alkali contained in the examined sample. To calculate the carbonate of soda as anhydrous caustic soda, it is multiplied by 0·5849; to calculate it as hydrate of soda, it is multiplied by 0·7547; to calculate the carbonate of potassa as anhydrous caustic potassa, it is multiplied by 0·6817; to calculate it as hydrate of potassa, it is multiplied by 0·8119.

It will be readily seen that this object may also be attained simply by the method given in § 221, by determining in *one* weighed sample the carbonic acid at once, in *another* after previous treatment with carbonate of ammonia.

The same object may also be attained in the volumetric way, by the following process:—

Weigh off $\frac{3}{10}$ equivalent, of potash accordingly, 20·73 grammes, of soda 15·9 grammes; dissolve in water, in a flask holding 300 c.c., fill up to the mark, shake, allow the fluid to deposit, out of contact of air, and take out two portions of 100 c.c. each. Determine in the one portion the total quantity of the carbonated and caustic alkali, as directed § 220; the number of c.c. of standard acid used expresses the amount of caustic alkali + alkaline carbonate, expressed in per-cents of the latter. Transfer the other portion to a measuring flask holding 300 c.c., add 100 c.c. of water, then solution of chloride of barium as long as a precipitate forms, add water up to the mark, shake, let deposit out of contact of air, then filter rapidly through a dry filter, measure off 100 c.c. of the filtrate—which now contains caustic baryta in corresponding quantity to the caustic potassa present in the sample—add some litmus tincture, then standard nitric acid to acid reaction. Neutralize the excess of acid, by standard solution of soda, and deduct the number of c.c. used of the latter from the number of c.c. of standard acid added; the difference expresses the number of c.c. of the standard acid required by the caustic baryta. Multiply this by 3 (as only $\frac{1}{3}$ of the second portion has been employed in the experiment); the result gives the per-centage amount of caustic alkali, expressed as carbonate of soda or potassa. Deduct the weight obtained from the result of the estimation of the first portion; the difference gives the quantity of carbonate of potassa or soda present in the analysed sample in that form of combination. To calculate the caustic alkali in the anhydrous or hydrated state, it is only necessary to multiply the quantities of carbonate of potassa or soda found by the number given in the first method.

D. ESTIMATION OF CARBONATE OF SODA IN PRESENCE OF CARBONATE OF POTASSA.

Soda being much cheaper than potash, is often used to adulterate the latter. The common alkalimetric methods not only fail to detect this adulteration, but they give the admixed soda as carbonate of potassa. Many processes have been proposed for estimating in a simple way the soda contained in potash, but not one of them can be said to satisfy the requirements of the case.*

The following tolerably expeditious process, however, gives accurate results:—Dissolve 6·25 grms. of the gently ignited potash in water, filter the solution into a quarter-litre flask, add acetic acid to feebly acid reaction, apply a gentle heat until the carbonic acid is expelled, then add to the fluid, while still hot, acetate of lead, drop by drop, until the formation of a precipitate of sulphate of lead *just* ceases; allow the mixture to cool, add water up to the mark, shake, let deposit, filter through a dry filter, and transfer 200 c.c. of the filtrate, corresponding to 5 grms. of potash, to another ¼-litre flask. Add sulphuretted hydrogen water of proper strength up to the mark, and shake. If the acetate of lead has been carefully added, the fluid will now smell of sulphuretted hydrogen, and no longer contain lead; in the contrary case, sulphuretted hydrogen gas must be conducted into it. After the sulphide of lead has subsided, filter through a dry filter. Evaporate 50 c.c. of the filtrate, corresponding to 1 grm. of potash, with addition of 10 c.c. of hydrochloric acid, of 1·10 sp. gr., in a weighed platinum dish, to dryness, then cover the dish, heat, and weigh; the weight found expresses the total quantity of chloride of potassium and chloride of sodium given by 1 grm. of potash. Estimate the potassa and soda now severally by the indirect method, determining the chlorine volumetrically (§ 141, I., *b*). For the calculation of the results, see § 200.

3. ESTIMATION OF ALKALINE EARTHS BY THE ALKALIMETRIC METHOD.

§ 223.

Alkaline earths, in the caustic state or in the form of carbonates, may also be estimated by means of a standard acid. Standard sulphuric acid may be used for the estimation of magnesia; standard nitric acid for that of baryta, strontia, and lime. To prepare 1 litre of the latter, measure off, by means of a burette, with caoutchouc connector and compression clamp, 20 c.c. of pure nitric acid, of about 1·04 sp. gr.; color slightly red with litmus tincture, and add standard solution of soda (or, at least, solution of soda of known strength, determined by standard sulphuric or standard oxalic acid), until the color just changes to blue. Repeat the same experiment. Suppose 20 c.c. of the acid have required

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* Comp. "Handwörterbuch der Chemie," Second Edition, I. 443.

24 c.c. of the soda solution, add to every 20 volumes of the acid 4 volumes of water. For the proper way of effecting the dilution, see § 215, *aa*, *a* (Preparation of Standard Sulphuric Acid). After diluting, measure off 20 c.c., and neutralize with the standard solution of soda, of which it must now take exactly 20 c.c.

Before using these standard fluids in actual experiments, test them as follows:—

Weigh off about 1·5 grm. of chemically pure, gently ignited carbonate of soda, cooled under the exsiccator, dissolve, in a flask, in 50—100 c.c. of water, and add tincture of litmus until the color of the fluid is slightly blue; now add, from the burette, the nitric acid to be tested, until the color changes to violet. Boil for some time, then add again nitric acid until the color changes to onion red; heat to boiling, add nitric acid up to the next divisional line, then standard solution of soda, until the color of the fluid just changes to blue. Deduct the volume added of the soda solution from that of the nitric acid used; the difference shows the quantity of nitric acid neutralized by the weighed sample of pure carbonate of soda.

Now, if the proportion

$$1000 : 53 \text{ (1 eq. NaO, CO}_2\text{)} :: \text{the number of c.c. of acid used} : x,$$

gives, as x, a number of grammes equal or nearly equal to that of the weighed sample of pure carbonate of soda, the nitric acid is of the correct standard, *i.e.*, it contains in 1000 c.c. 54 grammes of anhydrous acid, and 1000 c.c. of it saturate accordingly 1 eq. of an alkali or an alkaline earth.

If the alkaline earth to be estimated is in the caustic state, weigh off a definite quantity, add water, then, from a burette with compression clamp, nitric acid, until solution is effected, and the fluid, colored with litmus, appears reddish; now add soda solution until the color just changes to blue; deduct the soda solution added from the nitric acid, and calculate by the proportion

$$\begin{gathered}1000 \text{ c.c.} : 76{\cdot}59 \text{ (eq. of baryta)—}51{\cdot}67 \text{ (eq. of strontia)—}28 \text{ (eq. of} \\ \text{lime)—}20 \text{ (eq. of magnesia),} \\ :: \end{gathered}$$

the number of c.c. of the acid used : x baryta, strontia, lime, or magnesia.

Should there be a failure the first time in determining the exact point at which the fluid turns blue, upon addition of the last drop of standard soda solution, add another c.c. of the acid, and then again solution of soda until the color just changes to blue.

In the case of carbonates of the alkaline earths, heat a weighed quantity of the sample, in a flask, with water; then add, from the burette with compression clamp, small portions of nitric acid, until solution is effected, and the fluid, colored with litmus, appears reddish. Heat to boiling, shake the liquid, and continue boiling for some minutes, to expel the carbonic acid completely from the fluid and the flask; then add standard solution of soda until the color just changes to blue—1000 c. c. of the standard nitric acid correspond to 98·59 grms. of carbonate of baryta, 73·67 grms. of carbonate of strontia, 50 grammes of carbonate of lime, or 42 grammes of carbonate of magnesia.

By weighing off the $\frac{1}{10}$ or $\frac{1}{20}$ equivalents of the caustic or carbonated alkaline earths (H = 1), expressed in grammes, the necessity of a calculation of the results is altogether dispensed with ; in the former case, the number of c.c., in the latter that of half c.c. used of the standard acid, expresses the per-centage amount of caustic or carbonated earth contained in the analysed sample.

4. Chlorimetry.

§ 224.

The chloride of lime, or bleaching powder of commerce, is a mixture of hydrate of lime with hypochlorite of lime and chloride of calcium ; in pure chloride of lime, the two latter ingredients are always present in the proportion of 1 equivalent of the one to 1 equivalent of the other. The action of an acid upon chloride of lime effects the liberation of the whole of the chlorine present, since

$$\mathrm{Ca\,O,\,Cl\,O + Ca\,Cl + 2\,S\,O_3 = 2\,Ca\,O,\,S\,O_3 + 2\,Cl.}$$

The bleaching powder of commerce varies exceedingly in the amount of chlorine which it yields when treated with acids. Now, as the commercial value of this article, which is extensively manufactured and sold, depends entirely upon the proportional amount of chlorine which it contains, it was very natural that chemists should endeavor to devise some simple method of determining the available amount of chlorine in any given sample of bleaching powder. The various methods proposed with the view of effecting this object have collectively received the name of "*Chlorimetry.*"

The number of chlorimetrical methods that have been proposed is so great, that I cannot give all of them, but must confine myself to a description of those which are distinguished either for the facility of the process or for the accuracy of the results, or which deserve mention from the circumstance that they are commonly employed. In the description of the several methods, I shall have occasion to speak of their respective advantages and defects.

Before proceeding to the description of the chorimetrical methods, I have to remark that the results of the examination of chloride of lime are usually expressed in two different ways. Whilst the scientific chemist gives the per-centage amount of available chlorine contained in a sample of chloride of lime by weight, the commercial article is valued and sold by chlorimetrical degrees. This latter method, devised by *Gay-Lussac*, expresses how many litres of chlorine gas of 0° C. (32° F.), at 0·76 met. atmospheric pressure (29·9° bar.), are contained in 1000 grammes of chloride of lime.

However, as we know that 1 litre of chlorine gas of 0° C. and 0·76 met. bar. weighs 3·17763 grammes, it is easy to convert the results by measure into results by weight, and *vice versâ*.

Thus, for instance, a sample of chloride of lime of 90° contains 3·17763 × 90 = 285·986 grammes of chlorine in 1000 grammes, consequently 28·59 in 100 ; and a sample containing 34·2 per cent. by weight of chlorine, contains 107·6°, since, as 100 grammes contain 34·2 grammes of chlorine, 1000 grammes contain 342,

$$\text{and } \frac{342}{3{\cdot}1776} = 107{\cdot}6 \text{ litres.}$$

PREPARATION OF THE SOLUTION OF CHLORIDE OF LIME.

§ 225.

The solution is prepared alike for all methods, and this is done best in the following manner:—

Weigh off 10 grammes, triturate finely with a little water, add gradually more water, stir the mixture, let the grosser particles subside, and pour the supernatant liquid into the measuring flask, which must hold 1 litre; triturate the deposit again with water, and rinse the contents of the mortar carefully into the flask; fill the latter to the litre mark, shake the milky fluid, and examine it at once in that state, *i. e.*, without allowing it to deposit; and every time, before measuring off a fresh portion, shake again. The results obtained with this turbid solution are much more constant and accurate than those arrived at in cases where, as is usually recommended, the fluid has been allowed to deposit, and the experiment made with the supernatant clear portion alone. The truth of this may readily be proved by making two separate experiments, one with the decanted clear fluid, and the other with the residuary turbid mixture. Thus, for instance, in an experiment made in my own laboratory, the decanted clear fluid gave 22·6 of chlorine, the residuary mixture 25·0, the uniformly mixed turbid solution 24·5.

1 c.c. of the solution of chloride of lime so prepared corresponds to 0·01 grm. of chloride of lime.

A. *Method of Gay-Lussac* (slightly modified).

§ 226.

Gay-Lussac's method, which till lately was employed in most manufactories, is based upon the circumstance that the contact of chlorine with arsenious acid, in presence of water, gives rise to the formation of arsenic acid and hydrochloric acid:—

$$\text{As O}_3 + 2\text{ Cl} + 2\text{ HO} = \text{As O}_5 + 2\text{ HCl}.$$

One equivalent of arsenious acid = 99, requires accordingly 2 equivalents of chlorine = 70·92, for its conversion into arsenic acid; or, in other terms, 100 parts by weight of chlorine oxidize 139·6 parts of arsenious acid. Consequently, the amount of a solution of chlorine required to convert a definite quantity of arsenious acid into arsenic acid, indicates at once the proportional amount of chlorine present in that solution. The arsenious acid is best used in solution: it is prepared of definite strength as follows:—

a. Preparation of the Solution of Arsenious Acid.

Dissolve 13·96 grammes of pure arsenious acid in solution of potassa or soda, in a litre flask, dilute the solution, add hydrochloric acid to strongly acid reaction, then fill up with water to the litre-mark, and shake; 10 c.c. of the solution contain 0·1396 of arsenious acid, corresponding to 0·1 grm. of chlorine.

b. The Process.

Measure off with the pipette 10 c.c. of the solution of arsenious acid (*a*) transfer to a beaker, and dilute with water; add hydrochloric acid to strongly acid reaction; color the fluid blue with a drop of solution of sulphate of indigo, and add the solution of chloride of lime made according to the directions of § 225, drop by drop, with constant stirring, until the blue color has nearly disappeared. Add now another drop of solution of indigo, and then again solution of chloride of lime, until the fluid suddenly altogether loses its color, which the addition of a very small drop of solution of indigo fails to restore.

The amount of solution of chloride of lime used contained 0·1 grm. of chlorine. Suppose 40 c.c. have been used : as every cubic centimetre corresponds to 0·01 grm. of chloride of lime, the per-centage amount of chlorine by weight in the chloride of lime is found by the following proportion :—

$$0{\cdot}40 : 0{\cdot}10 :: 100 : x; \quad x = 25\ ;$$

or, by dividing 1000 by the number of c.c. used of the solution of chloride of lime.

This method, indeed, gives satisfactory results; but it requires some practice to hit the exact point when the arsenious acid is fully converted into arsenic acid; moreover, the process is liable to be vitiated by the disengagement of a little chlorine. The latter defect becomes more serious if, as is commonly done, a more concentrated solution of chloride of lime is used (see Analytical Notes and Experiments, No. 96).

B. *Penot's Method.*[*]

§ 227.

This method also is based upon the conversion of arsenious acid into arsenic acid; but the conversion is effected in an alkaline solution. Iodide of starch paper is employed to ascertain the exact point when the reaction is completed.

a. Preparation of the Iodide of Starch Paper.

Stir 3 grammes of potato starch in 250 c.c. of water, boil with stirring, add a solution of 1 grm. of iodide of potassium and 1 grm. of crystallized carbonate of soda, and dilute to the volume of 500 c.c. Moisten fine white (unsized) paper with this fluid, and dry.

b. Preparation of the Solution of Arsenious Acid.

Dissolve 4·436 grammes of pure arsenious acid and 13 grammes of pure crystallized carbonate of soda, in 600—700 c.c. of water, with the aid of heat, let the solution cool, and then dilute with water to the volume of 1 litre. Each cubic centimetre of this solution contains 0·004436 grm. of arsenious acid, corresponding to 1 c.c. of chlorine gas of 0° C. (32° F.) and 0·76 met. atmospheric pressure.[†]

As arsenite of soda in alkaline solution is liable, when exposed to access of air, to be gradually converted into arsenate of soda (see § 142,

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[*] "Bulletin de la Société Industrielle de Mulhouse," 1852, No. 118. *Dingler's* "Polytech. Journal," 127, 134.

[†] *Penot* gives the quantity of arsenious acid as 4·44 ; but I have corrected this number to 4·436, in accordance with the numbers which are at present assumed to represent the proper equivalents of the substances, and the correct weight of a litre of chlorine gas—after the following proportion :—
70·92 (2 equ. of chlorine) : 99 (1 equ. of AsO_3) :: 3·17763 (weight of a litre of chlorine gas) : x ; $x = 4{\cdot}436$, *i.e.* the quantity of arsenious acid which 1 litre of chlorine gas converts into arsenic acid.

1, *b*, *bb*), *Penot's* solution should be kept in small bottles with glass stoppers, filled to the top, and a fresh bottle used for every new series of experiments.

c. The Process.

Measure off, with a pipette, 50 c.c. of the solution of chloride of lime prepared according to the directions of § 225; transfer to a beaker, and add, slowly, and at last drop by drop, the solution of arsenious acid (*b*), from a burette holding 50 c.c., with constant stirring, until a drop of the mixture produces no longer a blue-colored spot on the iodized paper; it is very easy to hit the point exactly, as the gradually increasing faintness of the blue spots made on the paper by the fluid dropped on it, indicates the termination of the reaction, and warns the operator to confine the further addition of the solution of arsenious acid to a single drop at a time. The number of ½ c.c. used of the acid indicates directly the number of chlorimetrical degrees (*i.e.* the number of litres of chlorine gas contained in 1 kilogramme of the examined sample), as the following calculation shows: suppose you have used 40 c.c. of solution of arsenious acid, the solution of chloride of lime contains in 50 c.c., 40 c.c. of chlorine gas. Now, these 50 c.c. correspond to 0·5 grm. of chloride of lime; and, accordingly, as they contain 40 c.c. of chlorine gas, 1000 grammes contain 80,000 c.c. = 80 litres. This method gives very constant and accurate results, and appears to be particularly well suited for use in manufacturing establishments where there is no objection, on the score of danger, to the employment of arsenious acid.

Fr. Mohr ("Lehrbuch der Titrirmethode," I., 322) suggests the employment of his method of determining chlorine in the free state (see § 142, 1, *b*), for the estimation of chlorine in chloride of lime. A definite quantity of the chloride of lime solution is measured off, and solution of arsenite of soda added from a burette, until a drop of the mixture no longer produces blue spots on iodide of starch paper; starch paste is then added, and the excess of arsenite of soda finally determined by standard iodide solution. This method gives, indeed, accurate results, but the process is not so simple as *Penot's*.

C. *Otto's Method.*

§ 228.

The principle of this method is as follows:—

Two equivalents of sulphate of protoxide of iron, when brought into contact with chlorine, in presence of water and free sulphuric acid, give 1 equivalent of sulphate of sesquioxide of iron, and 1 equivalent of HCl, the process consuming 1 equivalent of chlorine.

$$2\,FeO,SO_3 + SO_3 + HO + Cl = Fe_2O_3,\,3\,SO_3 + HCl.$$

Two equivalents of $FeO,SO_3 = 152$, or, calculated as crystallized sulphate of protoxide of iron,

$$2\,(FeO,SO_3,HO + 6\,aq) = 278$$

correspond to 35·46 of chlorine, or, in other terms, 0·7839 grm. of crystallized sulphate of protoxide of iron correspond to 0·1 grm. of chlorine.

The sulphate of protoxide of iron required for these experiments is best prepared as follows:—

Take iron nails, free from rust, and dissolve in dilute sulphuric acid, applying heat in the last stage of the operation; filter the solution, still hot, into about twice its own volume of spirit of wine. The precipitate consists of

$$\mathrm{Fe\,O, S\,O_3 + H\,O + 6\,aq.}$$

Collect upon a filter, wash with spirit of wine, spread upon a sheet of blotting paper, and dry in the air. When the mass smells no longer of spirit of wine, transfer to a bottle and keep this well corked. Instead of sulphate of protoxide of iron, sulphate of protoxide of iron and ammonia (§ 65, 4) may be used. 0·1 grm. of chlorine peroxidizes 1·1055 grm. of this double sulphate.

The Process.

Dissolve 3·1356 grammes (4 × 0·7839 grm.) of the precipitated sulphate of protoxide of iron, or 4·422 grammes (4 × 1·1055 grm.) of sulphate of protoxide of iron and ammonia, with addition of a few drops of dilute sulphuric acid, in water, to the volume of 200 c.c.; take out, with a pipette, 50 c.c., corresponding to 0·7839 grm. of sulphate of protoxide of iron, or 1·1055 grm. of sulphate of protoxide of iron and ammonia, dilute with 150—200 c.c. of water, acidify with pure hydrochloric acid, and add, from a burette holding 50 c.c., the well shaken solution of chloride of lime, prepared according to the directions of § 225, until the sulphate of protoxide of iron is completely converted into sulphate of sesquioxide. To know the exact point when the peroxidation is completed, sprinkle a number of drops of a solution of ferricyanide of potassium on a clean plate, and, when the operation is drawing to an end, apply some of the mixture with a stirring rod to one of the drops on the plate, and observe whether it produces a blue precipitate; repeat the experiment after every fresh addition of two drops of the solution of chloride of lime. When the mixture no longer produces a blue precipitate in the solution of ferricyanide of potassium on the plate, read off the number of volumes used of the solution of chloride of lime. As the amount of solution of chloride of lime used contained 0·1 grm. of chlorine, the calculation is made exactly as in § 226.

This method also gives very satisfactory results, provided always that the salts of protoxide of iron are perfectly dry and free from sesquioxide.

Modifications of Otto's Method.

a. Instead of the solution of sulphate of protoxide of iron, a solution of protochloride of iron, prepared by dissolving pianoforte wire in hydrochloric acid (according to the directions given § 112, *b*, 2, *a*, *a*, *aa*), may be used with the best results. If 0·6316 of pure metallic iron, or 0·6335 of fine pianoforte wire, which may be assumed to contain 99·7 per cent. of iron, are dissolved to the volume of 200 c.c., the solution so prepared contains exactly the same amount of iron as the solution of sulphate of protoxide usually employed in *Otto's* process—that is to say, 50 c.c. of it correspond to 0·1 grm. of chlorine. But as it is not always convenient to weigh off a definite quantity of iron wire, the following course of proceeding may be pursued in preference: weigh off, accurately, about 0·15 grm. of iron, dissolve, dilute the solution to about 200 c.c., oxidize the iron with the solution of chloride of lime prepared according to the directions of § 225, and calculate the chlorine by the proportion

56 : 35·46 : : the quantity of iron used : x;

the x found corresponds to the chlorine contained in tho amount used of the solution of chloride of lime. This calculation may be dispensed with by the application of the following formulæ, which are calculated with due regard to the carbon in the pianoforte wire.

1. Multiply the weight of the pianoforte wire by 6313, and divide the product by the number of cubic centimetres used of the solution of chloride of lime: the result expresses the per-centage amount of chlorine by weight; or,

2. Multiply the weight of the wire by 19863, and divide the product by the number of cubic centimetres used of the solution of chloride of lime: the result expresses the chlorimetrical degrees of the chloride of lime (the number of litres of chlorine gas contained in 1 kilogramme of the examined sample).

This method gives very good results. I have described it here principally because it dispenses altogether with the use of standard fluids. It is therefore particularly well adapted for occasional examinations of samples of chloride of lime, and also by way of control.

b. Instead of directly oxidizing the protoxide or protochloride of iron by the chloride of lime, you may also proceed as follows:—Weigh off, accurately, about 0·3 grm. of pianoforte wire, dissolve to protochloride, and dilute the still strongly acid solution, to 200 or 300 c.c.; add slowly, from a burette, 50 c.c. of the solution of chloride of lime, prepared according to the directions of § 225, stir the fluid during the addition of the chloride of lime, and lastly determine, by means of permanganate of potassa, the quantity of iron which still remains in the state of protoxide or protochloride (§ 112). By this means the quantity of iron which has been peroxidized by the chloride of lime is ascertained, and from this you may calculate, by the formulæ given in *a*, the per-centage amount or chlorimetrical degrees of chlorine contained in the examined sample. The results are very accurate.

D. *Bunsen's Method.*

Pour 10 c.c. of the solution of chloride of lime, prepared according to the directions of § 225 (containing 0·1 of chloride of lime), into a beaker, and add about 6 c.c. of the solution of iodide of potassium, prepared according to the directions of § 146 (containing 0·6 of KI); dilute the mixture with about 100 c.c. of water, acidify with hydrochloric acid, and determine the liberated iodine as directed § 146. As 1 equivalent of iodine corresponds to 1 equivalent of chlorine, the calculation is easy. This method gives excellent results. (Compare Analytical Notes and Experiments, No. 96.)

I cannot recommend *C. Nöllner's* gravimetric method of estimating the chlorine in chloride of lime ("Annal. d. Chem. u. Pharm.," 95, 113), which is based upon the decomposition of the chloride of lime by hyposulphite of soda, and the determination of the sulphuric acid as sulphate of baryta. The results obtained by this method, in a series of experiments in my own laboratory, differed considerably according to the greater or less quantity of hyposulphite of soda used, and were altogether unsatisfactory. *Knop's* doubts of the accuracy of this method ("Pharm. Centralbl.," 1855, 656,) received the fullest confirmation by the results of these experiments.

5. ANALYSIS OF MANGANESE ORES.

§ 229.

The native ores of manganese (as well as the artificial product prepared from residues of chloride of manganese) are mixtures of binoxide of manganese with lower oxides of that metal, and with sesquioxide of iron, clay, &c.; they also invariably contain moisture, and often also hydration water. Now, as the commercial value of manganese ores depends entirely upon the amount of binoxide (or, more correctly expressed, of available oxygen) which they contain, it is a matter of the greatest interest for the manufacturer and merchant to ascertain this. By "available oxygen" we understand the excess of oxygen contained in a manganese ore, over the 1 equivalent combined with the metal to protoxide; upon treating the ore with hydrochloric acid, an amount of chlorine is obtained equivalent to this excess of oxygen. 1 equivalent of this available oxygen corresponds to 1 equivalent of binoxide of manganese, since $MnO_2 = MnO + O$.

Some years ago *De Vry* ("Annal. d. Chem. u. Pharm.," 61, 249) called attention to the fact that the discrepancies but too often observed in the results of the analyses of the same manganese ore by different chemists, are attributable principally to the variable amount of moisture in the several samples, and that the process employed for drying the samples intended for analysis is therefore a matter of the highest importance. Having since bestowed much time and attention upon this subject (see *Dingler's* Polyt. Journ., vol. 135, page 277), I can recommend the following process as best suited for preparing samples of manganese ores for analysis.

I. DRYING THE SAMPLE.

All analyses of manganese ores proceed of course upon the supposition that the sample selected is a fair average specimen of the ore. A portion of an average sample, reduced to a tolerably fine powder, is generally sent for analysis to the chemist; in the case of new lodes, however, a number of samples, taken from different parts of the mine, are also occasionally sent. If, in the latter case, the average composition of the ore is to be ascertained, and not simply that of the several samples, the following course of proceeding must be resorted to: crush the several samples of the ore in an iron mortar to coarse powder, and pass the whole of this through a rather coarse sieve. Mix uniformly, then transfer a sufficiently large portion of the coarse powder to a steel mortar, reduce to a fine powder, and pass the whole of this through a fine sieve. Mix the powder obtained by this second process of pulverization most intimately; take about 8—10 grammes of it, and triturate this, in small portions at a time, in an agate mortar, to an impalpable powder. Average samples are generally already sufficiently fine to require only the last operation.

Now, as regards the temperature best suited for the absolute removal of all moisture, without the least risk of loss of hydration water, the results of my experiments (see Analytical Notes and Experiments, No. 97) have shown that 248° F. is the proper temperature for drying samples of manganese ores intended for analysis. The best way would be to employ the drying disk described in § 31 (Fig. 36), exposing the finely powdered sample, in one of the disks, to a temperature of 248° F. for 1½ hours. But, as there appears to be at present an almost universal understanding in the manganese trade, to limit the drying temperature to 212° F., the fine powder is exposed, in a shallow copper or brass pan, for 6 hours to the temperature of boiling water, in a water-bath (Fig. 26). In laboratories where it is often necessary to dry a number of samples at the same time, it is found advantageous to use copper vessels, of the form of rather flat square boxes, with 4, 6, 12, or more, little drying cases placed inside on racks, so as to be surrounded on all sides by boiling water or steam.

When the sample has been dried according to these instructions, it is introduced, still hot, into glass tubes 12—14 centimetres long, and 8—10 millimetres wide; these tubes are then corked and allowed to cool.

In laboratories where whole series of analyses of different ores are of frequent occurrence, it is advisable to number the drying pans and glass tubes, and to transfer the samples always from the pan to the tube of the corresponding number.

II. Estimation of the Bixoxide in Manganese Ores.

§ 230.

Of the many methods that have been proposed for the examination of manganese ores, I select three as the most expeditious and accurate. The first is more particularly adapted for technical examinations.

A. *Fresenius and Will's Method.*

The principle upon which this method is based has been applied already by *Berthier* and *Thomson.*

The following remarks will serve to explain it.

a. If oxalic acid or an oxalate is brought into contact with binoxide of manganese, in presence of sulphuric acid in excess, sulphate of protoxide of manganese is formed, and carbonic acid evolved, as the oxygen, which we may assume to exist in the binoxide of manganese in combination with the protoxide of the metal, combines with the oxalic acid, and thus converts the latter into carbonic acid.

$$Mn\,O_2 + S\,O_3 + C_2\,O_3 = Mn\,O,\,S\,O_3 + 2\,C\,O_2.$$

Each equivalent of available oxygen or, what amounts to the same, of binoxide of manganese = 43·574, gives 2 equivalents of carbonic acid = 44.

b. If this process is performed in a weighed apparatus from which nothing except the evolved carbonic acid can escape, and which, at the same time, permits the complete expulsion of that acid, the diminution of weight will at once show the amount of carbonic acid which has escaped, and consequently, by a very simple calculation, the quantity of binoxide contained in the analysed manganese ore. As 44 parts by weight of carbonic acid correspond to 43·574 of binoxide of manganese, the carbonic acid found need simply be multiplied by 43·574, and the product divided by 44, or the carbonic acid may be multiplied by

$$\frac{43.574}{44} = 0{\cdot}99032,$$

to find the corresponding amount of binoxide of manganese.

c. But even this calculation may be avoided by simply using in the operation the exact weight of ore which, if the latter consisted of pure binoxide, would give 100 parts of carbonic acid.

The number of parts or volumes evolved of carbonic acid expresses, in that case, directly the number of parts of binoxide contained in 100 parts of the analysed ore. We have seen in *b* that 99·032 is the number required. Suppose the experiment is made with 0·99032 grm. of the ore, the number of centigrammes of carbonic acid evolved in the process expresses directly the per-centage amount of binoxide contained in the analysed manganese ore. Now, as the amount of carbonic acid evolved from 0·99032 grm. of manganese would be rather small for accurate weighing, it is advisable to take a multiple of this weight, and to divide afterwards the number of centigrammes of carbonic acid evolved from this multiple weight by the same number by which the unit has been multiplied. The multiple which answers the purpose best for superior ores is the triple, = 2·971; for inferior ores, I recommend the quadruple, = 3·961, or the quintuple, = 4952.

The analytical process is performed in the apparatus illustrated in Fig. 140, and which has been described also in § 139.

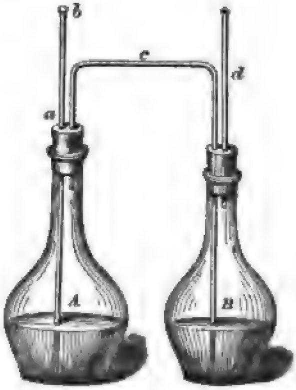

Fig. 140.

The flask A should hold, up to the neck, about 120 c.c.; B about 100 c.c. The latter is half filled with sulphuric acid; the tube *a* is closed at *b* with a little wax stopper, or a very small piece of caoutchouc tubing, with a short piece of glass rod inserted in the other end.

Place weights representing 2·971, or 3·961, or 4·952 grm.—according to the quality of the ore—in a watch-glass, and tare the latter most accurately on a delicate balance; then remove the weights from the watch-glass, and pour in the fine manganese powder from the tube, very cautiously, with the aid of a gentle tap with the finger, until the equilibrium is exactly restored. Transfer the weighed sample, with the aid of a card, to the flask A, add 5—6 grammes of pure neutral oxalate of soda, or about 7·5 grammes of pure neutral oxalate of potassa, in powder, and as much water as will fill the flask to about one-third. Insert the cork into A, and place the apparatus in equilibrium on a strong but delicate balance, by means of small shot, and lastly tinfoil, not placed directly on the balance, but in an appropriate vessel, which, after noting the tare, is kept under a glass jar. Try whether the apparatus closes air tight (see § 139, II. *e, a, aa*). Then make some sulphuric acid flow from B into A, by applying suction to *d*, by means of a caoutchouc tube. The evolution of carbonic acid commences immediately in a steady and uniform manner. When it begins to slacken, draw over a fresh portion of sulphuric acid into A, and repeat this until the manganese ore is completely decomposed, which, if the sample has been very finely pulverized, requires at the most about 5 minutes. The complete decomposition of the analysed ore is indicated, on the one hand, by the cessation of the disengagement of carbonic acid, and its non-renewal upon the influx of a fresh portion of sulphuric acid into A; and, on the other hand, by the total disappearance of every trace of black powder from the bottom of A.*

Now draw over some more sulphuric acid from B into A, to heat the fluid in the latter, and expel the last lingering traces of carbonic acid; remove the wax stopper, or india-rubber tube, from *b*, and apply gentle suction to *d* until the air drawn out tastes no longer of carbonic acid. Let the apparatus cool, then replace it on one scale of the balance, the tare on the other, and restore the original equilibrium. The number of centigramme weights added, divided by 3, 4, or 5, according to the multiple of 0·99032 grm. used, expresses the per-centage amount of binoxide contained in the analysed ore.

In experiments made with definite quantities of the ore, weighing in an open watch-glass cannot well be avoided, and the dried manganese is thus exposed to the chance of a re-absorption of water from the air, which of course tends to interfere, to however so trifling an extent, with the accuracy of the results. In very precise experiments, therefore, the best way is to analyse an indeterminate quantity of the ore, and to calculate the carbonic acid afterwards from the results by the proportion given in *b*. For this purpose, one of the little corked tubes, filled with the dry pulverized ore, is accurately weighed, and about 3 to 5 grammes (according to the quality of the ore) of the powder are transferred to the flask A. By now re-weighing the tube, the exact quantity of ore in the flask is ascertained. To facilitate this operation, it is advisable to scratch on the tube, with a file, marks indicating, approximately, the several quantities required for the analysis, according to the quality of the ore.

With proper skill and patience on the part of the operator, and a delicate balance and correct weights, this method gives most accurate and corresponding results, differing in two analyses barely to the extent of 0·2 per cent. In my own laboratory, I make it a rule to reject results differing by more than 0·2 per cent., in two experiments, and to repeat the analysis.

Some ores of manganese contain carbonates of the alkaline earths, which of course necessitates a modification of the foregoing process. To ascertain whether carbonates of the alkaline earths are present, boil a sample of the pulverized ore with water, and add nitric acid to see whether effervescence from the escape of carbonic acid will take place. If so, either determine the carbonic acid in a separate sample as directed § 139, II., *e*, and subtract the acid found, calculated upon the quantity of ore used for estimating the binoxide from the acid obtained in the latter process; or, modify the analytical process as follows: Introduce the weighed sample as usual into the flask A, then fill the latter about $\frac{1}{3}$ with dilute sulphuric acid; allow to stand at rest, with occasional agitation, until all effervescence has completely ceased; then apply a gentle heat to expel the last traces of carbonic acid. Introduce about 3 grammes of pounded oxalic acid of commerce into a small glass tube, and suspend this by a thread in A. Weigh the apparatus, and let the little tube drop into the fluid in A, which will at once induce decomposition of the manganese, and consequently the evolution of carbonic acid. Continue and terminate the process in the usual way.

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* If the manganese ore has been pulverized in an iron mortar, a few black spots (particles of iron from the mortar) will often remain perceptible.

B. *Bunsen's Method.*

Reduce the ore to the very finest powder, weigh off about 0·4 grm., introduce this into the small flask *d*, illustrated in Fig. 65, § 130, and pour pure fuming hydrochloric acid over it; conduct the process exactly as in the analysis of chromates. Boil until the ore is completely dissolved and all the chlorine expelled, which is effected in a few minutes. Each equivalent of iodine separated corresponds to 1 equivalent of chlorine evolved, and accordingly to 1 equivalent of binoxide of manganese.

In skilful hands, this method gives very accurate results. Instead of determining the chlorine by *Bunsen's* method, *Mohr's* method, described § 142, 1, *b*, may be used for the purpose.

C. *Estimation of the Binoxide in Manganese Ores by means of Iron.*

Dissolve, in a small long-necked flask, placed in a slanting position, about 1 gramme of pianoforte wire, accurately weighed, in moderately concentrated pure hydrochloric acid; weigh off about 0·6 grm. of the sample of manganese ore, in a little tube, which then drop into the flask, with its contents, and heat cautiously, until the ore is dissolved. 1 equivalent of binoxide of manganese converts 2 equivalents of dissolved iron from the state of proto- to that of sesquichloride. When complete solution has taken place, dilute the contents of the flask with water, let cool, rinse into a beaker, and determine the iron still remaining in the state of protochloride by solution of permanganate of potassa (§ 112, 2). Deduct this from the weight of the wire employed in this process; the difference expresses the quantity of iron which has been converted by the oxygen of the manganese from protochloride to sesquichloride.* This difference, multiplied by $\frac{43 \cdot 574}{56} = 0 \cdot 7781$, gives the amount of binoxide in the analysed ore. This method also, if carefully executed, gives very accurate results. Compare Analytical Notes and Experiments, No. 98. But it is better suited for scientific experiments than technical analyses, as, owing to the comparative smallness of the quantity of substance operated upon, much greater accuracy of weighing, &c., is required than in A. Instead of metallic iron, weighed quantities of pure sulphate of protoxide of iron (§ 228), or of sulphate of protoxide of iron and ammonia, may be used.

III. ESTIMATION OF MOISTURE IN MANGANESE.

§ 231.

In the purchase and sale of manganese, the ore is generally assumed to contain a certain amount of moisture, within certain limits, which must not be exceeded. In estimating this moisture, the same temperature should be employed, as a rule, at which the drying of the samples intended for analysis is effected (§ 229, I.).

As the amount of moisture in an ore may be altered by the operations of crushing and pulverizing, the experiment should be made with a sample of the mineral which has not yet been subjected to these processes. The drying must be continued until no further diminution of weight is observed; at 212° F., this takes about 6 hours, at 248° F., generally only $1\frac{1}{2}$ hours. If the moisture in a manganese ore is not to be estimated on the spot, but in the laboratory, a fair average sample of the ore should be forwarded to the chemist in a perfectly dry, well-corked bottle.

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* In very precise experiments, the weight of the iron must be multiplied by 0·997, since pianoforte wire may always be assumed to contain about 0·003 impurities.

IV. ESTIMATION OF THE AMOUNT OF HYDROCHLORIC ACID REQUIRED FOR THE COMPLETE DECOMPOSITION OF A MANGANESE ORE.

§ 232.

Different manganese ores, containing the same amount of available oxygen, or, as it is usually expressed, of binoxide, may require very different quantities of hydrochloric acid to effect their decomposition and solution, so as to give an amount of chlorine corresponding to the available oxygen in them ;—thus, an ore consisting of 60 per cent. of binoxide of manganese and 40 per cent. of sand and clay, requires only 2 equivalents of hydrochloric acid to 1 equivalent of available oxygen; whereas ores containing lower oxides of manganese, sesquioxide of iron, or carbonate of lime, require much larger proportions of hydrochloric acid.

The quantity of hydrochloric acid required to effect the complete decomposition and solution of a manganese ore may be determined by the following process :—

Determine the strength of 10 c.c. of hydrochloric acid, of about 1·10 sp. gr., by means of solution of sulphate of copper and ammonia (§ 216). Warm 10 c.c. of the same acid with a weighed quantity (about 1 grm.) of the sample of manganese ore under examination, in a small long-necked flask, with a glass tube, about 3 feet long, fitted into the neck. Attach the flask in a position that the tube is directed obliquely upwards, and then gently heat the contents. As soon as the manganese is decomposed, apply a somewhat stronger heat for a short time, to expel the chlorine which still remains in solution ; but carefully avoid continuing the application of heat longer than is absolutely necessary, as it is of importance to guard against loss of hydrochloric acid. Let the flask cool, and, when cold, dilute the contents with water, and determine the free hydrochloric acid remaining by solution of sulphate of copper and ammonia. Deduct the quantity found from that originally present; the difference expresses the amount of hydrochloric acid used to effect the decomposition of the manganese ore.

6. ANALYSIS OF COMMON SALT.

§ 233.

I select this example to show how to analyse, with accuracy and tolerable expedition, salts which, with a predominant principal ingredient, contain small quantities of other substances.

a. Reduce the salt by trituration to a uniform powder, and put this into a stoppered bottle.

b. Weigh off 10 grammes of the powder, and dissolve in a beaker by digestion with water ; filter the solution into a measuring flask holding 500 c.c., and thoroughly wash the small residue which generally remains. Finally fill the flask with water up to the mark, and shake the fluid.

If small, solid, white grains of sulphate of lime are left on dissolving the salt, reduce them to powder in a mortar, add water, let the mixture digest for some time, decant the clear supernatant fluid on to a filter, triturate the undissolved deposit again, add water, &c., and repeat the operation until complete solution is effected.

c. Ignite and weigh the dried insoluble residue of *b*, and subject it to a qualitative analysis, more especially with a view to ascertain whether it is perfectly free from sulphate of lime.

d. Of the solution *b*, measure off successively the following quantities:—

For *e.*	50 c.c.	corresponding to	1	grm. of common salt.
„ *f.*	150 c.c.	„ „	3	„ „ „
„ *g.*	150 c.c.	„ „	3	„ „ „
„ *h.*	50 c.c.	„ „	1	„ „ „

e. Determine in the 50 c.c. measured off, the *chlorine* as directed § 141, I., *a* or *b*.

f. Determine in the 150 c.c. measured off, the *sulphuric acid* as directed § 132, I., 1.

g. Determine in the 150 c.c. measured off, the lime and magnesia as directed § 154, B, 4 (**30**).

h. Mix the 50 c.c. measured off, in a platinum dish, with about ¼ c.c. of pure concentrated sulphuric acid, and proceed as directed § 98, 1. The neutral residue contains the sulphates of soda, lime, and magnesia. Deduct from this the quantity of the two latter substances as resulting from *g*; the difference is sulphate of soda.

i. Determine in another weighed portion of the salt, the water as directed § 35, *a*, *a*, at the end.

k. Bromine and other bodies, of which only very minute traces are found in common salt, are determined by the methods described in the analysis of mineral waters.

7. Analysis of Gunpowder.[*]

§ 234.

a. Estimation of the Moisture.—Weigh between watch-glasses about 2 grammes of the finely pulverized gunpowder, and dry at 212° F., until no further diminution of weight is observed.

b. Determination of the Nitrate of Potassa.—Place an accurately weighed quantity (about 5—6 grammes) on a filter dried at 212° F., but moistened again with water before the powder is placed on it; add to the powder on the filter as much water as it will absorb, and, after some time, repeatedly pour small quantities of hot water upon it until the nitrate of potassa is completely dissolved. When this is effected, dry the contents of the filter completely at 212° F., and weigh (§ 50). On the other hand, evaporate the solution of the nitrate of potassa in a weighed platinum dish, and determine the residue as directed in § 97, 2. The diminution of weight of the gunpowder and the increase of weight of the dish must exactly correspond, as both express the quantity of the nitrate of potassa.*

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[*] As regards the determination of the sp. gr. of gunpowder, I refer to *Heeren's* paper on the subject, in "Mittheilungen des Gewerbevereins für Hannover," 1856, 168—178; "Polyt. Centralbl.," 1856, 1118.

c. Determination of the Sulphur.

α. In the Dry Way (*Gay-Lussac*).

Mix 1 part (about 1—1·5 grm.) of the finely triturated powder with the same quantity of pure anhydrous carbonate of soda (free from sulphuric acid), add 1 part of pure nitrate of potassa and 6 parts of dry pure chloride of sodium; mix most intimately, and heat the mixture in a platinum crucible until the combustion is completed, which is indicated by the white color of the mass. Dissolve in water, acidify the solution with hydrochloric acid, and precipitate with chloride of barium the sulphuric acid formed by the oxidation of the sulphur (§ 132, I., 1).

β. In the Humid Way.

Oxidize 2 or 3 grammes of the powder with concentrated pure nitric acid and chlorate of potassa, adding the latter in small portions at a time, and keeping the fluid in a state of gentle ebullition. By this process both the sulphur and the charcoal are completely oxidized, and a clear solution is ultimately obtained; dilute this largely, and then determine the sulphuric acid in it as directed § 132, I., 1, taking particular care to have the sulphate of baryta quite pure. Should some charcoal be left after long continued digestion, this may also be filtered off and washed.

γ. In the Indirect Way.

Deduct the weight of the charcoal, determined as directed *d, α*, from the joint weight of the charcoal and sulphur; the difference expresses the weight of the latter.

d. Determination of the Charcoal.

α. Replace the weighed filter, with the charcoal and sulphur (see *b*) in the funnel, moisten with absolute alcohol, and extract the sulphur with a mixture of bisulphide of carbon and absolute alcohol. To promote the action of the solvent, heat the funnel by placing it in a larger one, and filling the space between with hot water. Wash finally with pure alcohol, dry the charcoal at 212° F., and weigh (*Marchand*).

β. Digest a weighed portion of the powder repeatedly with sulphide of ammonium, until all the sulphur is dissolved, and collect the charcoal on a filter dried at 212° F.; wash, first with water containing sulphide of ammonium, then with pure water, dry at 212° F., and weigh.

In cases where it is of importance to know the composition of the charcoal—*i. e.*, the amount of carbon, hydrogen, and oxygen contained in it—dry a sample of the charcoal previously dried at 212° F., at 374° F., noting the loss of weight (*Weltzien*), and subject the residue to an ultimate analysis. If the charcoal dried at 212° F. suffers a further diminution of weight at 374° F., deduct this, calculated in per-cents. of the powder, from the total amount of the charcoal, and add it to the moisture.

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* The nitrate of potassa may also be estimated in an expeditious manner, and with sufficient accuracy for technical purposes, by means of a hydrometer indicating the per-centage weight of the nitrate of potassa, if a weighed quantity of the gunpowder is dissolved in a definite amount of water. A method based upon the same principle, proposed by *Uchatius*, is given in the "Wiener acad. Ber.," X. 748; also "Ann. d. Chem. und Pharm.," 88, 395.

8. ANALYSIS OF NATIVE AND, MORE PARTICULARLY, OF MIXED SILICATES.*

§ 235.

The analysis of silicates which are completely decomposed by acids has been described in § 140, II., *a*; and that of silicates which are not decomposed by acids, in § 140, II., *b*. I have therefore here only to add a few remarks respecting the examination of mixed silicates, *i.e.* of such as are composed of silicates of the two classes (phonolites, clay slate, basalts, meteoric stones, &c.).

The silicate is very finely pulverized and dried at 212° F.; the dry powder is usually treated for some time, at a gentle heat, with moderately concentrated hydrochloric acid, and the mixture evaporated to dryness on the water-bath; the residue is moistened with hydrochloric acid, water added, and the solution filtered; it is often preferable, however, to digest the powder with dilute hydrochloric acid (of about 15 per cent.) for some days at a gentle heat, and then at once filter the solution. Which of the two ways it is advisable to adopt, and indeed whether the method here described, and which was first employed by *Chr. Gmelin* in the analysis of phonolites, may be resorted to, depends upon the nature of the mixed minerals. The more readily decomposable the one of the constituent parts of the mixture is, and the less readily decomposable the other, the more constant the relative proportion between the undissolved and the dissolved part is found to remain in different experiments; and, accordingly, the less the undissolved part is affected by further treatment with hydrochloric acid, the more safely may this method of decomposition be resorted to.

The process gives:—

a. A hydrochloric acid solution, containing the bases of the decomposed silicate in the form of metallic chlorides, which are separated and determined by the proper methods.

b. An insoluble residue, which contains, besides the undecomposed silicate, also the silicic acid of the decomposed silicate.

Wash the residue *b*, well with water, to which it is advisable to add a few drops of hydrochloric acid; transfer it, still moist, in small portions at a time, to a platinum dish containing a boiling solution of carbonate of soda (free from silicic acid); boil for some time, and filter off each portion, still very hot, through a weighed filter. Finally rinse the last particles of the residue which still adhere to the filter completely into the dish, and proceed as before. Should this operation not fully succeed, dry and incinerate the filter, transfer the ash to the platinum dish, and boil once more with the solution of carbonate of soda. Wash the residue, first with hot water, then—to ensure the removal of every trace of carbonate of soda which may still adhere to it—with water slightly acidified with hydrochloric acid, and finally again with pure water. Collect the washings in separate vessels (*H. Rose*).

Acidify the alkaline filtrate with hydrochloric acid, and determine in it the silicic acid proceeding from the silicate decomposed by the hydrochloric acid in the first process, as directed § 140, II., *a*. Dry the undissolved silicate and weigh. The difference gives the quantity of the dissolved silicate. Treat the undissolved silicate exactly as directed § 140, II., *b*.

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* Comp. "Qual. Anal.," § 203-206. The quantitative analysis must always be preceded by a minute and comprehensive qualitative analysis.

Silicates dried at 212° F. occasionally contain water, which is determined by igniting, in a platinum dish, a weighed sample of the dried silicate. To ascertain whether the expelled water proceeds from the silicate decomposed by hydrochloric acid, or from that which hydrochloric acid failed to decompose, a sample of the latter, dried at 212° F., is also ignited. Suppose, for instance, the mixed silicate under examination consists of 50 per cent. of silicate decomposed by hydrochloric acid, and 50 per cent. of silicate which hydrochloric acid fails to decompose; and that the latter contains 47 parts of anhydrous substance, and 3 parts of water; the determination of the water would give, for the mixed silicate 3 per cent., for the portion not decomposed by hydrochloric acid 6 per cent. Now, as 3 bears the same proportion to 6 as the undecomposed silicate (50 per cent.) bears to the mixed silicate (100 per cent.), it is clear that the silicate decomposed by hydrochloric acid gives no water upon ignition.

If the escaping aqueous vapors manifest acid reaction, owing to disengagement of hydrochloric acid gas, or terfluoride of silicon, mix the sample with 6 parts of finely triturated recently ignited oxide of lead, in a small retort, weigh, ignite, and weigh again. If the water passing over after this operation still manifests acid reaction, connect the retort with a small receiver containing water, and determine the hydrofluosilicic acid in the latter, after the termination of the process.

The undecomposed part of a mixed silicate occasionally contains charcoal, in which case it is the safest way to treat an aliquot part of it in a current of oxygen gas, and weigh the carbonic acid produced (§ 179).

Silicates often contain as impurities other minerals (magnetic iron, pyrites, apatite, carbonate of lime, &c.) which may sometimes be detected by the naked eye or a magnifying glass, but as often not. It would be rather a difficult undertaking to devise a generally applicable method for cases of this description; I therefore simply remark that it is occasionally found advantageous to treat the sample first with acetic acid, before subjecting it to the action of hydrochloric acid; this will more especially effect, without the least difficulty, the separation of the carbonates of the alkaline earths. For further information, I refer to "Journ. f. prakt. Chem.," 65, 199, where a paper on the subject will be found, giving a series of analyses made in my laboratory, by *Dollfus* and *Neubauer*.

If silicates contain small quantities of titanic acid, as is not unfrequently the case, care must be taken not to overlook this admixture. If the silicic acid has been separated by evaporating with hydrochloric acid, whether preceded or not by decomposition with carbonated alkali—and the evaporation has been effected on the water-bath, and with a sufficient quantity of hydrochloric acid, the titanic acid, or at least the far greater part of it, is found in the hydrochloric acid solution. On precipitating the latter with ammonia (§ 161, 4), igniting the precipitate, which contains sesquioxide of iron and alumina, and treating the ignited residue with hydrochloric acid, the greater part of the titanic acid is left undissolved, mixed with iron (*H. Rose*).

The quantity of the acid is, however, generally so small that the analyst must rest satisfied simply with the detection of its presence.

The separated silica may be tested for titanic acid, as follows:—

Dissolve in hydrofluoric acid, or treat with hydrofluoric gas (§ 140, II., *b*, *β*, *bb*); evaporate with sulphuric acid, expel the greater portion of the latter, add some sulphate of potassa, and keep the bisulphate of potassa formed in fusion for some time; dissolve the mass in cold water, and separate the titanic acid from the solution, previously filtered if necessary, as directed § 107.

The following process of analysing the several varieties of clay differs, in some respects, from the foregoing method.

9. ANALYSIS OF CLAYS.

§ 236.

The several varieties of clay, derived from the disintegration of felspar and other similar silicates, consist commonly of a mixture of true clay with quartz, or felspar sand, and often contain also free silicic acid, which may be dissolved out by means of boiling solution of carbonate of soda.

As it is of importance, for the various technical uses of clays, to know, not only the chemical composition of the different kinds, but also the compound parts of them separable by simple mechanical means, the chemical analysis of clays is generally preceded by a purely mechanical analysis.*

A. *Mechanical Analysis.*

The mechanical analysis of clays is intended to determine severally the quantities of coarse sand, impalpable sand, and fine clay, removable by elutriation, which they contain.

The process is effected with the aid of the elutriating apparatus recommended by *Fr. Schutze* ("Journ. f. prakt. Chem.," 47, 241) for the mechanical analysis of soils. It requires accordingly :—

a. A tall champagne glass, 20 centimetres deep, and 7 centimetres in diameter at the mouth, on which a brass ring is fastened, 15 millimetres broad, with a tube slightly inclined downward, proceeding from its side.

b. A funnel tube; the diameter of which should be 5 centimetres, the length of the tube 40 centimetres, by about 7 millimetres diameter, but drawn out at the point so as to leave at the mouth only a diameter of 1½ millim.

c. A vessel of, at least, 10 litres capacity, filled with water. The best material for this vessel is sheet zinc; it should have an aperture at the top for pouring in the water, and a lateral opening at the bottom with stopcock. It is placed upon a moveable support. The funnel tube is suspended from the cock by means of a small cord, so that the mouth opens over or in the funnel.

d. A dish, or large beaker, to receive the fluid running from the discharge tube.

Crush 30 grammes of the air-dried clay under examination; transfer to a porcelain dish, add 2 or 3 times the bulk of water, and boil for half an hour, with gentle rubbing with a pestle, to effect complete separation of the component parts of the clay. Allow the boiled mass to cool, and, when cold, wash the contents of the dish into the elutriating glass (*a*); open the cock of the vessel *c* a little, and insert the funnel tube, with the jet of water issuing from it, into *a*, taking care to place the extreme point of the tube some millimetres above the deepest part of the glass, which may be effected either by lowering the support of the vessel *c*, or by placing the elutriating glass higher. Regulate the cock so that the water always fills the funnel about half; under these circumstances the pressure of the water, *i.e.* the difference of level in the elutriating glass and the water vessel (*c*), is about 20 centimetres.

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* Compare my "Untersuchungen der wichtigsten Nassauischen Thone," "Journ. f. prakt. Chem.," 57, 65.

By the force of the jet of water the particles of clay are impetuously stirred up; but only the finest of them are thrown up sufficiently high to reach the lateral opening at the top of the glass, and thus to be carried off through the discharge tube, and conveyed into the dish or beaker (*d*); the coarse sand remains in the elutriating glass. When the water runs off almost clear from the discharge tube, shut the cock, remove the elutriating glass, and rapidly decant the still somewhat turbid supernatant liquid; then rinse the deposited sand with the aid of a washing bottle with jet directed upward, into a small dish, dry, ignite, and weigh.

Allow the elutriated turbid fluid in the dish or beaker (*d*) to settle for, at least, 6 hours; then decant the clear or still turbid supernatant fluid, wash the deposit, which is now sure to contain the whole of the fine sand, into the elutriating glass, and repeat the process of elutriation, restricting the flow of water from the vessel *c* to a mere dropping on to the side of the funnel, so that the column of water in the funnel tube stands only about 3 centimetres higher than in the elutriating glass; continue this operation until the water passing off through the discharge tube is quite clear, which generally takes 3 or 4 hours. Then shut off the cock, remove the elutriating glass, decant the supernatant fluid, rinse the deposit of fine sand, with the aid of a washing bottle, into a small dish, dry, ignite, and weigh.

Determine now the water in another weighed portion of the air-dried clay, by ignition, and estimate the clay by the difference. I have successfully employed this method in the analysis of the fat clay of *Ebernhahn*, and of the much poorer variety of *Hillscheid;* I obtained

	Clay of *Hillscheid.*	Clay of *Ebernhahn.*
Coarse sand	24·68	6·66
Fine sand	11·29	9·66
Clay	57·82	74·82
Water	6·21	8·86
	100·00	100·00

B. *Chemical Analysis.*

First Method.

a. Triturate the clay as finely as possible, dry a weighed sample of it for several days at 212° F., and calculate the moisture from the loss; keep the dried sample in a corked tube.

b. Fuse 1 or 2 grammes of the sample dried at 212° F., with carbonate of soda and potassa, and proceed exactly as directed § 140, II., *b.* Evaporate the hydrochloric acid solution, after removing the silicic acid by filtration, with addition of a few drops of nitric acid, until the greater portion of the free acid is expelled; then dilute with water, mix with pure carbonate of baryta in excess, and let the mixture digest for 24 hours in the cold, with repeated stirring; filter, and wash the precipitate, which consists of hydrate of alumina, a little hydrated sesquioxide of iron, and carbonate of baryta, first by decantation, then on the filter. Dissolve the washed precipitate in hydrochloric acid, remove the baryta from the solution by sulphuric acid, filter, wash, add the washings to the filtrate, and divide the latter into two equal portions, *a* and *β*.

a. Precipitate with ammonia, let stand for some time in a warm place, then filter; dry and ignite the precipitate, finally by means of the blast gas-lamp. Weigh the ignited precipitate, and multiply the weight by 2. The result is alumina + sesquioxide of iron.

β. Concentrate, reduce the sesquioxide of iron with zinc, determine the protoxide by solution of permanganate of potassa (§ 112, 2), calculate the iron for sesquioxide, and multiply the result by 2.

The alumina is = the result of *a* − the result of *β*. Mix the fluid filtered from the precipitate produced, by carbonate of baryta, without previous concentration, cautiously with sulphuric acid, filter off the sulphate of baryta, and wash until the washings are quite free from sulphuric acid. Concentrate the filtrate, but not sufficiently to cause separation of sulphate of lime; then separate the lime and magnesia as directed § 154, 4 (30).

c. Treat 1 or 2 grm. of the clay dried at 212° F., with hydrofluoric gas, as directed § 140, II., *b*, *β*, *bb*. After evaporating with sulphuric acid, and dissolving the residue with hydrochloric acid and water, add, cautiously, chloride of barium as long as a precipitate forms, then—without filtering—carbonate of ammonia and some ammonia. Let the precipitate deposit in the cold; filter, wash, evaporate the filtrate, ignite the residue, to expel the ammonia salts, and then proceed as directed § 153, 4, *a*, *δ* (18). By this process the magnesia is removed, together with any traces of lime and baryta which might still be present, and the chlorides of the alkali metals are obtained in the pure state; if potassa and soda are present, the chlorides are separated as directed § 152, 1, *a*.

d. Determine the water, in a weighed sample of the clay dried at 212° F., by long-continued ignition in a platinum crucible. The loss of weight shows the amount of water present in the analysed sample in a state of combination; but the result is generally a little too high, as many varieties of clay contain traces of organic matter, which are decomposed by ignition; and many evolve also trifling quantities of chloride of ammonium (compare Untersuchung der wichtigsten Nassauischen Thone, "Journ. f. prakt. Chemie," 57, 65).

The foregoing processes give the general composition of the clay. To ascertain also how much of the silicic acid formed exists in the analysed clay in combination with the bases (A), how much as hydrated acid (B), and how much as quartz sand, or as a silicate present in form of sand* (C), the following processes are required.

e. Heat a third portion (1—2 grm.) of the clay dried at 212° F., with an excess of sulphuric acid, mixed with some water, until the acid is driven off. Let the mixture cool, add water, wash the undissolved residue $(A+B+C)$, dry, ignite, and weigh; then treat with boiling solution of carbonate of soda, as directed § 235, *b*. Filter off the undissolved sand (C), wash, ignite, and weigh.

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* Felspar sand, for instance.

$$A+B+C-C=A+B.$$

If the weight of $A+B+C$ is equal to the total amount of silicic acid found in *b*, the sand is pure quartz sand; but if it is greater, the sand is not pure quartz sand, but consists of the more or less sandy powder of a silicate, *e.g.*, felspar sand; in the latter case, subtract $A+B$ from the total quantity of the silicic acid, and place the difference to the account of C.

f. To ascertain the amount of silicic acid which a boiling solution of carbonate of soda will remove from the clay (B), and which may be assumed to be present in the analysed clay as hydrated silicic acid, boil a somewhat larger weighed portion of the sample, dried at 212° F., repeatedly with solution of carbonate of soda, and determine the silicic acid in the filtrate by evaporation with hydrochloric acid.

$$A+B-B=A.$$

Second Method.

The analysis of clays composed of quartz sand, and of clay readily decomposed by sulphuric acid, may be effected by the following much less complicated method :—

a. Preparation for analysis, drying, and estimation of water, the same as in the first method.

b. Decompose about 2 grammes of the sample with sulphuric acid, as in *e* of the first method; remove the greater part of the sulphuric acid by evaporation, dilute with water, and filter off the silicic acid and sand; weigh; separate the silicic acid from the sand by solution of carbonate of soda, and finally determine the weight of the sand.

c. Add to the filtrate of *b*, cautiously, solution of nitrate of oxide of lead, taking care to avoid a notable excess; after several hours, filter off the sulphate of lead, wash, add the washings to the filtrate, then remove from the latter the last trace of lead by sulphuretted hydrogen, filter, evaporate the filtrate, finally in a small dish, and treat the residue as directed § 161, 5 (**101**). As clay rarely contains appreciable traces of manganese, this method (**101**) is reduced to a few simple operations.

10. ANALYSIS OF LIMESTONES, DOLOMITES, MARLS, &c.

As the minerals containing carbonate of lime and carbonate of magnesia play a very important part in manufactures and agriculture, the chemist is often called upon to analyse them. The analytical process differs according to the different object in view. For technical purposes, it is sufficient to ascertain the principal component parts; the geologist takes an interest also in the matter present in smaller proportions; whilst for the purposes of agricultural chemistry it is necessary not only to know the constituents, but the state of solubility, in different solvents, in which they are severally present.

I will give, in the first place, a process for effecting a complete and accurate analysis of limestones, dolomites, &c.; and, in the second place, the volumetric methods by which the carbonate of lime (and the carbonate of magnesia) may be determined. An accurate qualitative examination should always precede the quantitative analysis.

A. METHOD OF EFFECTING THE COMPLETE ANALYSIS OF LIMESTONES, DOLOMITES, ETC.

§ 237.

a. Reduce a large piece of the mineral to powder, mix this uniformly, and dry at 212° F.

b. Treat about 2 grammes of the powder, in a covered beaker, with dilute hydrochloric acid in excess, evaporate the mixture to dryness, in a platinum or porcelain dish, moisten the residue with hydrochloric acid, heat with water, filter on a dried and weighed filter, wash the insoluble residue, dry at 212° F., and weigh. The residue generally consists of separated *silicic acid, clay, and sand:* but it often contains also *organic matter.* The processes described in *d* will give more accurate information on these points.

c. Mix the hydrochloric acid solution with chlorine water, then with ammonia in slight excess, and let the mixture stand at rest for some time, in a covered vessel, at a gentle heat. Filter the precipitate, which contains—besides sesquioxide of iron, sesquioxide of manganese, and hydrate of alumina—the phosphoric acid which the analysed compound may contain, and, moreover, invariably traces of lime and magnesia; wash slightly, and redissolve in hydrochloric acid; heat the solution, add chlorine water, and then precipitate again with ammonia; filter the fluid from the precipitate, wash, dry, ignite, and weigh. For the estimation of the respective quantities of the several components of the precipitate, viz., *sesquioxide of iron, protosesquioxide of manganese, alumina, phosphoric acid,* see *g.*

d. Unite the fluids filtered from the first and second precipitates produced by ammonia, and determine the *lime* and *magnesia* as directed § 154, 4 (30).

e. If the limestone dried at 212° F. still gives *water* upon ignition, this is estimated best as directed § 36.

f. If the limestone contains no other volatile constituents besides water and carbonic acid, ignite with fused borax (§ 139, II., *d*), and subtract from the loss of weight suffered, the water found in *e*; the difference is carbonic acid. If this method is inapplicable, determine the carbonic acid as directed § 139, II., *e, a, bb.*

g. To effect the estimation of the constituents present in smaller proportion, as well as a more complete analysis of the residue insoluble in hydrochloric acid, and of the precipitate produced by ammonia, dissolve 20—50 grammes of the mineral in hydrochloric acid. As the evaporation to dryness of large quantities of fluid is always a tedious operation, gently heat the solution for some time, to expel the carbonic acid; then filter, through a weighed filter, into a litre flask, wash the residue, dry, and weigh. The weight will not quite agree with that of the residue in *b*, as the latter contains also that part of the silicic acid which here still remains in solution.

a. Analysis of the insoluble Residue.

aa. Treat a portion with boiling solution of pure carbonate of soda (§ 235, *b*); separate the silicic acid from the solution, and proceed as directed § 140, II., *a*; this process gives the quantity of that portion of the *silicic acid* contained in the residue, which is *soluble in alkalies.*

bb. Treat another portion as directed § 140, II., *b*, and deduct from the *silicic acid* found, the amount obtained in *aa.*

cc. If the residue contains *organic matter* (humus), determine, in a portion, the carbon by the method of ultimate analysis (§ 179, *b*). *Petzholdt*,* who determined by this method the coloring organic matter of several dolomites, assumes that 58 parts of carbon correspond to 100 parts of organic substance (humic acid).

dd. If the residue contains *pyrites*,† fuse another portion of it with carbonate of soda and nitrate of potassa; treat the fused mass with water, add hydrochloric acid to the solution, evaporate to dryness, moisten the residue with hydrochloric acid, gently heat with water, filter, determine the sulphuric acid in the filtrate, and calculate from the result the amount of pyrites present in the analysed sample.‡

β. Analysis of the Hydrochloric Acid Solution.

aa. Dilute the solution to the volume of 1000 cc., mix intimately, and divide into three parts, one of one-half, and the other two one quarter each; mix the half part with a small quantity of dilute sulphuric acid, concentrate by evaporation, then dilute again, and filter if necessary. The precipitate may contain sulphate of *baryta*, sulphate of *strontia*, and sulphate of lime, and also silicic acid. Treat it as directed § 209, 7, *b*.

Treat the filtrate of *aa* with sulphuretted hydrogen. If this produces a precipitate (may be of *sulphide of copper*), filter, and determine the metal or metals in it. Treat the filtrate, after expelling the sulphuretted hydrogen, with chlorine gas or chlorine water, and precipitate twice with ammonia (compare *c*). Wash the precipitate, dry, ignite, and weigh; then treat with fuming hydrochloric acid, which will leave most of the silicic acid undissolved. The solution generally contains *iron*, *manganese*, *alumina*, and *phosphoric acid*, which may be separated as directed § 209, 7, *b*, *bb*.

bb. One quarter (= 250 c.c.) of the dilute hydrochloric acid solution is used for the estimation of the alkalies. Mix with chlorine water, then with ammonia and carbonate of ammonia; after allowing the mixture to stand for some time, filter off the precipitate, evaporate the filtrate to dryness, ignite the residue in a platinum dish to remove the ammonia salts, and finally separate the magnesia from the alkalies by means of oxalic acid, as directed § 153, 4, δ (18). The reagents must be most carefully tested for fixed alkalies, and the use of glass and porcelain vessels avoided as far as practicable.

cc. Mix the last quarter of the hydrochloric acid solution with chloride of barium, and allow the mixture to stand for some time. If a precipitate of sulphate of baryta forms, determine this as directed § 132, I., 1.

h. As calcareous spar and Arragonites may contain *fluorides* (*Jenzsch*, "Pogg. Annal.," 96, p. 145), the possible presence of fluorine must not be disregarded in accurate analyses of limestones. Treat, therefore, a larger sample of the mineral with acetic acid until the carbonate of lime and carbonate of magnesia are decomposed; evaporate to dryness until the excess of acetic acid is completely expelled, and extract the residue with water (§ 138, I.). If fluorine is present, it may now easily be detected in the residue (see "Qual. Anal.," 5th Edition, § 147, 6; also foot-note to § 209, 13), and determine as directed § 166, 5.

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* "Journal f. prakt. Chem." 63, 194.

† Compare *Petzholdt* ("Journ. f. prakt. Chem.," 63, 194); *Ebelmen* ("Compt. rend.," 33, 681); *Deville* ("Compt. rend.," 37, 1001; "Journ. f. prakt. Chem.," 62, 81); *Roth* ("Journ. f. prakt. Chem.," 58, 84).

‡ If the residue contains sulphate of baryta or strontia, these compounds are formed again upon evaporating the soaked mass with hydrochloric acid; they remain accordingly on the filter, whilst the sulphuric acid formed by the sulphur of the pyrites, passes into the filtrate.

i. If the limestone under examination contains *chlorides*, treat a large sample with water and nitric acid, at a very gentle heat; filter, and precipitate the chlorine from the filtrate by solution of nitrate of silver.

k. It is often interesting for agriculturists to know the degree of solubility of a sample of limestone or marl in the weaker solvents. This may be ascertained by treating the sample first with water, then with acetic acid, finally with hydrochloric acid, and examining each solution and the residue (*C. Struckmann*, Analysis of Marls, "Annal. d. Chem. u. Pharm.," 74, 170).

l. To effect the separation of the caustic or carbonate of lime, in hydraulic limestone, from the silicates, *Deville* ("Compt. rend.," 37, 1001; "Journ. f. prakt. Chem.," 62, 81) proposes to boil with solution of nitrate of ammonia, which he stated would dissolve the caustic lime and carbonate of lime, without exercising a decomposing action on the silicates. *Gunning* ("Journ. f. prakt. Chem.," 62, 318) found, however that by this process the double silicates of alumina and lime are more or less decomposed, with separation of silicic acid. As yet no method is known by which the object here stated can be accomplished with any degree of accuracy; the best way, perhaps, is treating the sample with dilute acetic acid; *C. Knausz* ("Gewerbeblatt aus Würtemberg," 1855, No. 4; "Chem. Centralbl.," 1855, page 244) recommends hydrochloric acid.

B. VOLUMETRIC DETERMINATION OF CARBONATE OF LIME AND CARBONATE OF MAGNESIA (for technical purposes).

§ 238.

a. If a mineral contains only carbonate of lime, the amount of the latter may be estimated from the quantity of acid required to effect its decomposition, the method described in § 223* being employed for the purpose. Or the carbonic acid in the mineral may be determined, say by the method described in § 139, II., *e*, *a*, *bb*, and 1 equivalent of carbonate of lime = 50 calculated for each equivalent of carbonic acid = 22.

b. But if the analysed mineral contains, besides carbonate of lime, also carbonate of magnesia, the results obtained by either process give the quantity of carbonate of lime + carbonate of magnesia, the latter being expressed by its equivalent of carbonate of lime (*i.e.* 50 of carbonate of lime for 42 of carbonate of magnesia). The lime and magnesia must, therefore, still be determined separately, which may be effected by one of the two following methods:—

1. Mix the dilute solution of 2—5 grammes of the mineral with ammonia and oxalate of ammonia in excess, allow the mixture to stand for 12 hours, then filter, wash, and dry. Ignite the precipitate of oxalate of lime, together with the filter, and treat the carbonate of lime produced as directed § 223. This process gives the amount of lime contained in the analysed mineral; the magnesia is found by difference, after duly calculating the carbonate of lime upon carbonate of magnesia.

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* This method, with some slight differences, was first proposed by *Bineau*.

To obtain perfectly accurate results by this method, double precipitation is indispensable (see § 154, 4, *a*).

2. Dissolve 2—5 grammes of the mineral in the least possible excess of hydrochloric acid, and add a solution of lime in sugar water as long as a precipitate forms. By this operation the magnesia only is precipitated. Filter, wash, and proceed as directed § 223. Calculate the magnesia as carbonate of lime, and subtract the results from the total amount obtained in *b*; the difference expresses the quantity of carbonate of lime contained in the analysed mineral.

The method 2 is only adapted for the analysis of limestones containing but a small proportion of magnesia.

11. ANALYSIS OF IRON ORES.

The iron ores most commonly employed, and which the chemist is therefore most frequently called upon to examine, are, red hematite, brown hematite, bog iron, magnetic iron, and spathic iron ores. In some cases, a complete analysis of these ores is required; in others, simply a quantitative estimation of certain of the constituent parts (the iron, phosphoric acid, sulphuric acid, &c.); in others again, merely the determination of the iron.

A. METHODS OF EFFECTING THE COMPLETE ANALYSIS OF THE ORES.

§ 239.

I. RED HEMATITE.

This ore contains the iron as sesquioxide; beside this, some moisture is always present, and commonly also an admixture (insoluble in acids) of the matrix in which the ore occurs; often a little titanic acid, sometimes carbonates of the alkaline earths, and traces of an oxide of manganese are also found associated with it.

Reduce the ore to a very fine powder, and dry at 212° F.

a. Treat the powder with dilute nitric acid or dilute boiling acetic acid, to remove the admixture of carbonates of the alkaline earths which the ore may contain. Determine these (if any are present) in the solution obtained.

b. Ignite a sample of the powder, free from admixture of carbonates of the alkaline earths, first in the air, then in pure, dry, hydrogen gas, which is effected best in a small porcelain boat inserted in a porcelain tube (§ 160, 3 [69]), until the formation of water ceases. The loss of weight expresses the quantity of oxygen in the sesquioxide, from which the amount of the latter may be calculated.

c. Treat the residue with dilute hydrochloric acid. The iron dissolves, the admixture from the matrix is left. Filter, heat the filtrate, which generally already contains some sesquichloride of iron, with a fragment of zinc (§ 113, *b*, 2, *a*), best in a current of hydrogen gas (§ 149, II., *a*, *a*), until complete reduction is effected, and determine the iron finally by solution of permanganate of potassa (§ 112, *b*, 2, *a*). The result must agree with that of *b*; if the results of the two processes differ, that of *c* may generally be considered the more reliable of the two.

d. Dry, heat, ignite, and weigh the residue obtained in *c*, which contains the titanic acid if any is present. To detect and determine it, boil the residue, in a platinum crucible, with concentrated sulphuric acid, mixed with a little water. When the greater portion of the sulphuric acid has evaporated, dilute the residue largely with water, filter, and separate the titanic acid by long-continued boiling (§ 107).

e. The water may be determined by igniting a separate portion of the powder. If the ore contains carbonates of the alkaline earths, the carbonic acid of the latter escapes with the water.

II. BROWN HEMATITE.

This ore contains the iron, or the far greater part of it, as hydrated sesquioxide, and, besides, alumina and sesquioxide of manganese; often also small quantities of lime and magnesia, and of silicic acid (in combination with bases), phosphoric acid, and sulphuric acid, and always a larger or smaller admixture of quartz sand or gangue* insoluble in hydrochloric acid.

A complete and accurate analysis of this ore presents some difficulties. One of the following methods may be selected. The preliminary operations indispensable in all of them are the reduction of the ore to a fine powder, which is dried at 212° F., or under the exsiccator, and the ignition of a sample, to ascertain the amount of water. In the latter process, it must be borne in mind that, in presence of carbonates of the alkaline earths, or carbonate of protoxide of iron, the water must not be estimated from the loss of weight, but determined by direct weighing (§ 36).

a. Decomposition in the Dry Way. (This method is more particularly recommended for the analysis of ores containing only small quantities of silicic acid, alumina, lime, and magnesia.)

Fuse a weighed portion of the powder with three times its weight of carbonate of soda and potassa, and boil the fused mass with water until the soluble parts are dissolved; filter the solution from the residue, and well wash the latter.

aa. The *filtrate* contains, besides the excess of carbonate of soda, the soda salts of the acids present in the analysed ore (silicic acid, phosphoric acid, sulphuric acid, and, perhaps, also arsenic acid, chlorine, and fluorine); generally, however, the first three acids alone are present in an appreciable proportion.

Acidify the alkaline filtrate with hydrochloric acid and separate the silicic acid in the usual way (§ 140, II., *a*). Add to the filtrate a few drops of chloride of barium, allow to stand for 24 hours, and then filter off the precipitate of sulphate of baryta which may have formed. Remove the baryta from the filtrate by means of a few drops of dilute sulphuric acid, and then precipitate the phosphoric acid with magnesia, as directed § 134, I., *b*. Should arsenic acid be present, this must be removed by sulphuretted hydrogen, before the precipitation of the phosphoric acid.

bb. Dissolve the *residue* in hydrochloric acid, separate the silicic acid, which is generally present in this solution, as directed § 140, II., *a*, and treat the filtrate with sulphuretted hydrogen, to precipitate any traces of copper that might be present; then separate the iron, manganese, alumina, lime, and magnesia, by one of the methods given in § 161.

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* Besides these substances, which are generally found in brown hematite, traces of other bodies are often also detected by a searching analysis. Thus *A. Müller* ("Annal. d. Chem. u. Pharm.," § 86, 127) found in a variety of pea-iron ore (Carlshütte, near Alfeld) ponderable traces of potassa, arsenic acid, and vanadic acid, and imponderable traces of chromium, copper, and molybdenum.

b. Decomposition in the Humid Way.

Heat about 10 grammes of the finely pulverized mineral, in an obliquely placed flask, with concentrated hydrochloric acid, until complete decomposition is effected; evaporate on the water-bath to dryness, moisten the residue with hydrochloric acid, heat gently, dilute with water, filter into a measuring flask holding 250 c.c., and wash; dry, ignite, and weigh the undissolved residue; it consists of quartz sand or gangue, and liberated silicic acid. The latter may be separated and determined, by boiling the residue with a solution of carbonate of soda (§ 235, *b*).

The filtrate is diluted to the volume of 250 c.c., and then treated as follows:—

1. To determine the *sulphuric acid*, evaporate 50 c.c. until the greater part of the hydrochloric acid is removed, then dilute with about 200 c.c. of water, add chloride of barium, and let the mixture stand at least 24 hours; then filter off the trifling precipitate of sulphate of baryta which generally forms.

2. Determine, in another portion of 50 c.c., the *phosphoric acid*, by means of molybdate of ammonia (§ 134, I., *b*, β*). If arsenic acid is present, this must first be removed by sulphuretted hydrogen (§ 166, 1), as molybdic acid precipitates this acid also.

3. In another portion of 50 c.c., determine the *iron* volumetrically, by solution of permanganate of potassa, after previous reduction of the sesquioxide by boiling with zinc (§ 113, *b*, 2, *a*).

4. Treat another portion of 50 c.c. as directed § 161, 2 (96), to determine the *iron* once more, and also the *manganese*, *alumina*, and *alkaline earths*. As phosphoric acid (and arsenic acid, if present) pass into the precipitate produced by acetate of soda, regard must be had to the possible presence of these acids, in estimating the alumina by the difference. If the qualitative analysis has given ponderable traces of copper or arsenic acid, these substances must first be removed by sulphuretted hydrogen; in which case the reduced protoxide of iron is again peroxidized by nitric acid, before proceeding as above directed.

III. Bog Iron Ore.

Bog iron ore consists of a mixture of hydrated sesquioxide of iron with the basic salts of sesquioxide of iron with silicic acid, sulphuric acid, phosphoric acid, arsenic acid, crenic acid, apocrenic acid, and humic acid, and generally contains besides these, gangue, alumina, lime, and magnesia.

Reduce the ore to powder, and dry. Expose a portion of it, in an open platinum crucible, at first to a dull red heat, to burn the organic acids, then gradually for some time to an intense red heat, with the crucible placed in an oblique position. The loss expresses the amount of water and organic substances originally present in the ignited ore.

Treat another sample by one of the methods given in II.; the sample may previously be very gently ignited, only just sufficient to destroy the organic substances.

To detect and determine the organic acids, boil a larger portion of the finely pulverized ore with pure solution of potassa, until it is converted into a flocculent mass. Filter and treat the filtrate as directed § 209, 10.

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* The method described § 135, i., γ, may also be resorted to.

IV. Magnetic Iron Ore.

Magnetic iron ore contains the metal as protosesquioxide. Analyse the ore in the same way as the red hematite, and determine afterwards in a separate weighed portion, dissolved in hydrochloric acid, in a current of carbonic acid, the protoxide of iron by volumetric analysis, as directed § 112, *b*, 2, *a*.

V. Spathic Iron Ore.

Spathic iron ore contains carbonate of protoxide of iron, associated usually with carbonate of manganese and carbonates of the alkaline earths, and often mixed also with clay and gangue.

Reduce the mineral to powder and dry.

a. Determine the water as directed § 36.

b. Determine the carbonic acid as directed § 139, II., *e*, *α* or *β*.

c. Dissolve a third portion of the powder in hydrochloric acid, with addition of nitric acid. When complete decomposition has been effected, filter the fluid from the undissolved residue, and separate the bases in the filtrate as directed in II., *b*, 4, or by one of the methods given in § 161.

d. In a fourth portion of the powder, dissolved in hydrochloric acid, in a current of carbonic acid, determine the quantity of the protoxide of iron volumetrically, as directed § 112, *b*, 2, *a*.

e. If the residue insoluble in hydrochloric acid is considerable, proceed with it as directed § 235 (Analyis of Silicates).

B. Estimation of the Iron in Iron Ores.

§ 240.

This is now almost exclusively effected by means of *solution of permanganate of potassa.* Heat 0·5 grm. of the finely pulverized ore, dried in the air; or at 212° F., in a long-necked flask, placed obliquely, with concentrated hydrochloric acid until complete decomposition is effected; dilute with about 30 c.c. of water, reduce with zinc, and proceed exactly as directed § 113, *b*, 2, *a*.

2. In the supplement to §§ 112 and 113, *Fuchs's* indirect method of estimating iron ("Journ. f. prakt. Chem.," 17, 160) is stated to give neither accurate nor constant results. However, it would now appear, from two recent papers on the subject, one by *J. Löwe* ("Journ. f. prakt. Chem.," 72, 28), the other by *R. König* ("Journ. f. prakt. Chem.," 72, 36), that this unfavourable opinion was based upon erroneous data, and that the method, which I will now proceed to describe, is very suitable for technical purposes.

a. Common method (as described by *Löwe*, "Journ. f. prakt. Chem.," 72, 28).

If the ore intended for analysis is of a superior kind, take 1—1·5 grm., if an inferior ore, 2—3 grammes; reduce to very fine powder, and heat, in an obliquely placed long-necked glass flask of about 500 c.c. capacity, with strong hydrochloric acid; when all sesquioxide of iron is dissolved, add, gradually, small pieces of fused chlorate of potassa, until the fluid smells distinctly of chlorine, and continue heating until this smell is no longer perceptible. Dilute with water until the flask is half full, and then insert a sound cork, in which a glass tube, open at both ends, about 10 inches long, and not too narrow, is fitted air-tight; place the flask in a slanting position, and heat for, *at least*, 15 minutes to moderate boiling, to ensure the expulsion of every trace of chlorine and atmospheric air.

Whilst keeping the solution in *incessant ebullition*, open the cork, and suspend in the neck of the flask a strip of pure clean sheet copper, attached to a platinum wire, inserting the cork again so as to keep the wire in position; when the copper strip has become sufficiently hot to allow of its immersion in the fluid, without danger of spurting, open the cork again, let down the strip of copper horizontally to the bottom of the flask, so as to immerse it completely in the fluid; insert the cork now firmly, place the flask again in a slanting position, taking care to keep the fluid during this manipulation in *incessant*, though slow and moderate ebullition, and continue this until the iron in the solution is completely reduced, and appears, accordingly, *quite* colorless, or at least exhibits but a very inconsiderable and indistinct greenish tint. The object of the process is generally attained in about 2 hours, but the boiling may be continued for 3 or 4 hours without the *least* detriment to the accuracy of the results. The strip of copper must always remain completely covered by the fluid; it is for this reason that so large a quantity of water is added at first, as any subsequent additions would of course be quite impracticable.

The strip of copper should weigh about 6 grammes, it should be made of copper precipitated by galvanic action, and of the proper breadth and length to pass readily through the neck of the flask and lie at the bottom in a horizontal position. It is scoured clean with sand-paper, weighed, and then attached to the platinum wire.

When the reduction of the iron is completed, uncork the flask, promptly withdraw from the still boiling fluid the strip of copper, by means of the platinum wire; immerse in a beaker filled with distilled water, take out again, rinse by means of the washing bottle, dry completely between blotting paper, take off the platinum wire, weigh, and reckon for each equivalent of copper dissolved in the process, as indicated by the loss of weight of the strip, 1 equivalent of iron (see *Supplement* to §§ 112 and 113, *a*). The copper is found to have lost its original lustre in the process, and looks dull, but not blackish, as is generally the case if ordinary sheet copper is used.

In four analyses of chemically pure sesquioxide of iron, *J. Löwe* obtained by this process, severally, 99·7, 99·6, 99·6, 99·6 per cent. of sesquioxide of iron. *König's* process ("Journ. f. prakt. Chem.," 72, 36) is nearly the same as *Löwe's*. He recommends, however, to keep the strip of copper, after its removal from the boiling fluid, for some time in hot water, to ensure the removal of every particle of the solution which may have penetrated into the pores of the metal; then to remove the water by immersion in absolute alcohol, and the latter again by immersion in ether. He also recommends to wind platinum wire round the strip, which, besides accelerating the reduction, will prevent the scaling off of small particles of the copper, that might otherwise be caused by the bumping of the metal against the sides of the vessel during the process of ebullition. The results which *König's* obtained by this process, in a series of experiments, varied between 99·5 and 100·5 per cent.

b. Modified Process.

If the ore contains an appreciable proportion of titanic acid, *Fuchs'* process (*a*) requires certain modifications, for which I refer to the original paper on the subject ("Journ. f. Prakt. Chem.," 18, 495; see also *König*, "Journ. f. Prakt. Chem.," 72, 38), as cases of the kind are of comparatively rare occurrence. If the ore contains arsenic acid, the process is inapplicable, as a coating of blackish scales of arsenide of copper would form on the copper. The arsenic acid may be removed, however, by fusing the pulverized ore with carbonate of soda, and extracting the fused mass with water, dissolving the residue in hydrochloric acid, and treating the solution as in *a*.

12. Copper Pyrites.

§ 241.

This mineral contains copper, iron, sulphur, and generally also gangue. Whether it contains other metals, besides copper and iron, must be ascertained by a qualitative analysis.

The finely pulverized mineral is dried at 212° F.

a. The estimation of the sulphur is generally effected in the humid way, according to the directions given § 148, II., 2, *a*; but it may be effected also as directed § 148, II., 2, *b*, or in the dry way (§ 148, II., 1).

b. If nitric acid is used as oxidizing agent (§ 148, II., 2, *a*) the bases are either determined in a fresh sample of the mineral, or the excess of baryta is removed by sulphuric acid, the fluid evaporated, to expel the nitric acid as completely as possible, and the copper and iron are then finally separated by means of sulphuretted hydrogen (§ 162, A), or by hyposulphite of soda (§ 162, B, 4, *a*, 112).

But if the sulphur is estimated by fusion with nitrate of potassa and carbonate of soda (§ 148, II., 1), or the mineral in alkaline solution is decomposed by chlorine (§ 148, II., 2, *b*), the residual oxides of iron and copper are dissolved in hydrochloric acid, and then separated by one of the processes described. Which of these methods should be preferred, depends upon the presence of appreciable quantities of other metals besides copper and iron; if zinc blende is present, the first method is preferable; if arsenic, one of the two latter methods. In complicated cases, treatment with chlorine in the dry way is resorted to (§ 148, II., 1, *c*).

If the quantity of copper alone is to be determined, and no other metal precipitable by zinc is present, the mineral may be decomposed with hydrochloric acid and chlorate of potassa, the solution evaporated to dryness, the residue dissolved by hydrochloric acid and water, the solution filtered into a platinum dish, and the copper precipitated by zinc (§ 119, 2). Or *Schwarz's* volumetric method (§ 119, 4, *a*) may be employed; but, in effecting the reduction, care must be taken not to raise the heat above 176° F., at which temperature iron will not precipitate from a fluid containing a large proportion of alkaline tartrate. However, even supposing some iron to precipitate with the copper, this could exercise no adverse influence on the quantitative estimation of the latter metal.

13. Galena.

§ 242.

Galena, the most widely spread of the lead ores, frequently contains larger or smaller quantities of iron, copper, silver, and commonly also gangue, more or less insoluble in acids.

The best way of analysing it, is as follows :—

Reduce the ore to a fine powder, and dry at 212° F.

Oxidize a weighed quantity of the powder (1—2 grammes) with highly concentrated red fuming nitric acid, free from sulphuric acid (see § 148, II., 2, *a*, *a*; however, the ore is not exposed in a tube to the action of the acid). If the acid is sufficiently strong, the whole of the sulphur is oxidized. After heating gently for some time, dilute with water, filter, and wash the residue.

a. Dry the *residue*, ignite, and weigh (§ 116, 2). It consists of sulphate of lead, gangue undecomposed by the acid, silicic acid, &c. Heat the whole, or a fractional part, with hydrochloric acid to boiling; let the residuary sediment subside, and then decant the supernatant clear liquid on to a filter; pour a fresh portion of hydrochloric acid over the residue, boil again, let the residuary sediment subside, and decant, and repeat this operation until the sulphate of lead is completely dissolved; finally place the residue on the filter, and wash with boiling water until every trace of chloride of lead is removed; dry, ignite, and weigh. Subtract the weight found from that of the original residue: the difference expresses the quantity of sulphate of lead which the latter contained. Instead of using hydrochloric acid, the sulphate of lead may also be dissolved by heating with an aqueous solution of tartrate or acetate of ammonia and caustic ammonia; or it may be converted, first into carbonate of lead, by digestion with solution of carbonate of soda, and the washed carbonate of lead dissolved in dilute nitric acid.

b. Evaporate the *filtrate*, which still contains a small amount of dissolved sulphate of lead and also the other metals which may be present, nearly to dryness, to expel the excess of free nitric acid; dilute again with water. Should a small quantity of sulphate of lead remain undissolved, filter, and treat the washed sulphate, together with the principal amount, as directed in *a*. Test the filtrate for *silver*, with very dilute hydrochloric acid. If a precipitate forms, add a further quantity of the hydrochloric acid, if necessary, and let the turbid fluid stand for some time in a warm place, until the chloride of silver has subsided; then filter, wash the precipitate with boiling water, and determine the chloride of silver as directed § 115, 1. Determine the sulphuric acid which the filtrate may still contain, by means of a little chloride of barium, then precipitate with sulphuretted hydrogen. The precipitate may contain, besides sulphide of lead, sulphide of copper, and possibly also sulphides of other metals. These and the metals in the filtrate, which are precipitable by sulphide of ammonium, are separated by the methods given in Section V.

Calculate the proportion of sulphur both in the sulphate of lead (*a*) and in the sulphate of baryta (*b*), and add the results together: the sum gives the total quantity of the sulphur contained in the analysed ore.

DETERMINATION OF THE SILVER IN GALENA.

§ 243.

The foregoing method does not enable the assayer to determine very small quantities of silver* and the trifling traces of gold which, according to *Percy* and *Smith* ("Phil. Mag.," vii. 126), are often found in galena.

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* Argentiferous galena ores generally contain only between ½ to 3, rarely above 8 ounces of silver per cwt. (0·03 to 0·18, or 0·5 per cent.); and a great many contain even less than 0·03 per cent.

To effect this, it is, in the first place, necessary to produce a button, or bead, containing the whole or part of the lead of the galena, and the whole of the silver and gold, and then to separate the latter metals in the humid or dry way.*

PRODUCTION OF THE BUTTON OR BEAD.

1. *Methods suitable for poor Argentiferous Galena Ores.*

a. Mix 20 grammes of the finest pulverized galena with 60 grammes of anhydrous carbonate of soda and 6 grammes of nitrate of potassa, transfer the mixture to a hessian crucible, cover it with a layer, 8 mm deep, of decrepitated chloride of sodium, and fuse, finally at a bright red heat, so as to produce a fusible slag. Let the crucible cool slowly, then break it to pieces, flatten the button, which must be close and compact, on the anvil, and free it from all adherent impurities by boiling with water. By this process 75—78 per cent. of lead are obtained from pure galena, instead of 86·6 per cent., which the pure ore actually contains; but every particle of the silver is found in the button (*Berthier; Fresenius*). To understand the process, it must be borne in mind that the fusion of galena with carbonate of soda, out of contact of air, produces metallic lead and a slag consisting of sulphide of lead and sodium and sulphate of soda.

$$4\,NaO, CO_2 + 7\,PbS = 4\,Pb + 3\,(PbS, NaS) + NaO, SO_3 + 4\,CO_2.$$

The nitrate of potassa serves to decompose the sulphur salt, separate the lead, and oxidize the sodium and the sulphur.

b. Mix 20 grammes of pulverized galena with 30 grammes of black flux (prepared by deflagrating 1 part of nitrate of potassa with 2½ parts of bitartrate of potassa) and 5—6 grammes of very small iron nails, and fuse the mixture in a hessian crucible, at a bright red heat. The ore is decomposed, the sulphur combining partly with the iron, partly with the alkali, and the lead separates in a state of fusion. Let the crucible cool, then break it to pieces, and proceed as in *a.* Take care that the lead incloses no nails. *Berthier* obtained by this process 72—79 per cent. of lead.

2. *Method more particularly suitable for rich Argentiferous Galena Ores.* (Refining assay.†)

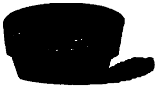

Fig. 141.

The process requires pots of baked fire-clay (see Fig. 141), and a properly constructed assay furnace, with good draught.‡

4 grammes of the finely pulverized ore are mixed with 32 grammes of lead free from silver (which may be prepared in laboratories, most conveniently by precipi-

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* *Ch. Mène* ("Compt. rend.," 45, 484; "Polyt. Centralbl.," 1858, 78) has recently determined the silver in various galena ores by the following process. He heated a mixture of 20 grammes of the pounded ore with a mixture of 1 part of nitric acid and 4 parts of water, filtered off the sulphur, precipitated the filtrate with an excess of ammonia, filtered off the precipitate rapidly, washed with ammoniated water, mixed the filtrate with an excess of hydrochloric acid, and a little nitric acid, and weighed the precipitated chloride of silver. I place no confidence in this method, as chloride of silver is not insoluble in solution of chloride of ammonium, which is formed in large quantity in this process. I should recommend to precipitate the ammoniacal fluid with sulphide of ammonium, dissolve the washed precipitate in nitric acid, dilute largely, and precipitate with dilute hydrochloric acid.

† Compare *Bodemann* and *Kerl's* "Anleitung zur Probirkunst," Clausthal, 1856, p. 287.

‡ For a detailed description of a properly constructed assay furnace, see the above work.

tating solution of acetate of lead with zinc), in a test-pot, so that about half of the lead is mixed with the ore, the remaining half covering the mixture in a uniform layer. According to the nature of the impurities mixed with the ore, certain fluxes are also added, viz., borax, quartz, or glass. Borax is added in the case of ores containing much lime, magnesia, zinc, &c.; this quantity varies with the amount of the extraneous bases in the ore, and may occasionally rise to from 2—5 grm. If the ore contains quartz or silicates, no borax is added, or only a little, up to 0·5 grm. If the ore contains little or no silicic acid, in combination or in the free state, a very small proportion of glass or quartz is added.

32 grammes of lead to 4 grammes of ore may be considered the normal proportion; however, for ores containing a considerable amount of zinc blende or pyrites, 48 or 64 grammes of lead are used to 4 grammes of ore; and the presence of compounds of copper or tin necessitates the use of a still larger proportion of lead. The test-pots, properly charged, are introduced into the muffle (see Fig. 145), previously heated to bright redness, and the mouth of the latter is closed with pieces of red-hot charcoal, to accelerate the fusion of the lead. The lead fuses, whilst the lighter ore floats on the surface and passes off; the fumes evolved during this process of roasting differ according to the nature of the escaping products; sulphur forms light grey, zinc dense white, arsenic grayish-white, antimony bluish fumes.

After 15 or 20 minutes a fusible slag forms, which completely surrounds the fused metal at the edges, dense fumes of lead rising at the same time from the surface of the latter. With refractory samples, it takes occasionally as long as 35 minutes before this point is attained, and the fused metal presents a smooth surface.

The pieces of charcoal are now removed from the mouth of the muffle, and the dampers of the furnace closed. The lead coming in contact with the air begins to oxidize at once; this oxidation is allowed to proceed until the scoriæ entirely or nearly cover the metal; when this point is attained, the heat is once more raised, for about 5 minutes, to a high degree of intensity, to increase the fluidity of the slag. The process of scorification generally occupies half an hour, but never more than an hour.

The test-pots are now taken out of the muffle with tongs about 3 feet long, of the form shown in Fig. 142, and the metal and slag poured into the opening of a heated iron or copper mould.* The alloy obtained must form a single button, separating readily from the slag. The button is hammered on the anvil into the proper shape to be readily laid hold of with the tongs shown in Fig. 143, and placed on the cupel, without projecting over the edge; these tongs are also about 3 feet long.

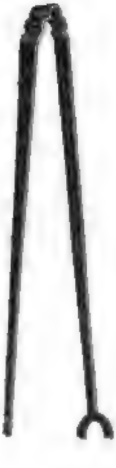

Fig. 142.

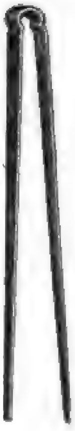

Fig. 143.

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* Consisting of a plate with hemispherical cavities of 3 cub. cent. diameter, coated with red or white chalk.

In the process here described the ore is roasted at first, and litharge produced, which then decomposes the metallic sulphides, with formation of sulphurous acid and separation of the metals; the oxide of lead formed dissolves also the earths and other oxides and removes them as slags.

DETERMINATION OF THE SILVER IN THE ARGENTIFEROUS LEAD BUTTON.

This may be effected either in the humid or in the dry way. In chemical laboratories, the want of proper assay furnaces generally compels the selection of the former; whereas in metallurgical laboratories the dry way is invariably resorted to.

1. *Methods by the Humid Way.*

a. Dissolve the clean button in moderately dilute nitric acid free from chlorine, dilute the solution largely, and add some very dilute hydrochloric acid or solution of chloride of lead. Put the turbid fluid in a warm place, until the chloride of silver has subsided, then filter, wash thoroughly with boiling water, and determine the silver finally as directed § 115, 1—the results are satisfactory ("Analytical Notes and Experiments," No. 99).

b. Dissolve the button in nitric acid, and treat the solution as directed § 163, 11 (139, *Pisani's* method), taking care to employ for the precipitation of the lead, sulphate of potassa or soda perfectly free from hydrochloric acid or metallic chlorides.

2. *Method by the Dry Way* (Cupellation*).

This operation requires small cups of compressed bone-ash, called *cupels* (see Fig. 144), which may now be readily purchased. Though 1 part by weight of the porous mass of the cupel can absorb the oxide of 2 parts by weight of lead, yet it is always considered the safer way to calculate only upon the absorption of the oxide of 1 part of lead; the weight of the button should, therefore, not greatly exceed that of the cupel.

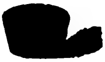
Fig. 144.

When the muffle (see Fig. 145) is sufficiently heated to show half of the bottom in a state of white heat, the cupels are introduced empty, and gradually pushed back until they are in a state of bright redness; for it is necessary for the success of the process that the alloy of lead and silver should fuse quickly, as otherwise small particles of lead are apt to stick to the upper edge of the cupel. If the furnace is heated to the proper degree, the separation of the silver from the lead will speedily begin; if not, pieces of red-hot charcoal are placed in the mouth of the muffle, to accelerate the process. As soon as the surface of the lead is in motion, the dampers of the furnace are closed, and only a single piece of charcoal is left in the mouth of the muffle. The great point now is to effect the complete separation of the silver from the lead at the proper degree of heat. If the temperature is raised too high, particles of the silver will be absorbed by the cupel along with the

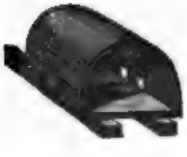
Fig. 145.

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* The description of this interesting and important operation is taken from *Bodemann* and *Kerl's* "Anleitung zur Probirkunst," Clausthal, 1856.

litharge. On the other hand, if the temperature is not sufficiently high, refrigeration of the assay is the consequence; the oxidation of the lead ceases, and an imperfectly melted oxide is formed, which the cupel cannot absorb. And even though the temperature of the furnace should afterwards be raised sufficiently high to make the refrigerated assay resume its ordinary train, the results of the process are no longer reliable.

If the process is properly conducted, the lead fumes rising from the cupels slowly ascend to the middle of the muffle, the cupels are at a reddish-brown heat, and rings of imperfect small crystals of oxide of lead are formed at the edges of the cupels. If the lead fumes disappear immediately above the cupels, whilst the latter are at a bright red heat, and no crystals are formed at the edges, the heat is too stroug. If, on the other hand, the fumes ascend to the vault of the muffle, and the edges of the cupels look dark brown, the temperature is too low, and there is danger of refrigeration of the assay.

Towards the end of the operation the temperature must be raised, as the bead becomes more refractory with the increase of the proportion of silver in it, and the last particles of lead require a higher temperature for their oxidation and absorption by the cupel. Care must be taken, however, not to raise the heat prematurely or suddenly, and never to a degree of intensity sufficient to remelt the crystals. When the process is drawing to a close, there remains only a very thin film of litharge on the silver, which imparts an iridescent appearance to the surface; this also suddenly disappears at last, leaving the silver perfectly bright. The phenomenon of the total disappearance of the last coloured particles of the oxide of lead is called the *lightning*, or *fulguration*. The silver bead is now allowed to cool very slowly, to prevent the *spitting* of the metal, which the impetuous escape of the oxygen gas absorbed by the silver in a state of fusion would otherwise occasion.

The bead must readily separate from the cupel, from which it is removed by means of pincers; its form must be hemispherical or round; the upper surface silvery white and brilliant; the lower surface, after brushing, clean and silvery white, though not lustrous. Beads with projecting ridges or knobs on the lower surface, arising from fissures or depressions in the cupel, must be rejected, as the projecting parts always contain lead. The properly cleaned beads are weighed. If the lead used is not absolutely free from silver, this must be determined, and the results of the assay corrected accordingly. The weighed silver bead may be tested for gold, and the latter, if necessary, be determined as directed § 164, B (144).

Silver assays by cupellation are invariably attended with a small loss of the precious metal. *Burbidge Hambly's* experiments ("Chem. Gaz.," 1856, p. 185) have shown that this loss becomes greater in the same ratio as the proportion of the lead to the silver is increased. In an assay made with 1 part of silver to 1 of lead, the loss of silver was 5·5 in 1000 parts of silver; in an assay made with 1 part of silver to 15 parts of lead, 16·2; with 1 part of silver to 35 parts of lead, 18·8 in 1000.

14. ANALYSIS OF ZINC ORES.

§ 244.

A. CALAMINE AND SILICATE OF ZINC ORE.

The former of these ores consists of carbonate of zinc, which commonly contains larger or smaller admixtures of protoxide of iron, protoxide of manganese, oxide of lead, oxide of cadmium, lime, magnesia, and silicic acid; the latter consists of silicate of zinc, which may contain admixtures of silicates of lead, binoxide of tin, protoxide of manganese, sesquioxide of iron, &c.

The ore is reduced to a fine powder, and dried at 212° F.

a. A portion of the powder is treated as directed § 140, II., *a*—that is, the silicic acid is separated in the usual way. As the silicic acid generally contains sand or undecomposed gangue, it must be separated from this by boiling with a solution of carbonate of soda (§ 235, *b*).

b. In treating the residue with hydrochloric acid and water, 10 parts of acid are used to about 25 parts of water (see § 162, A, β).

c. The solution obtained by this process is precipitated with sulphuretted hydrogen, and the metals which may be thrown down by that reagent are separated by the proper methods described in Section V. In very accurate experiments, the precipitate produced by sulphuretted hydrogen must be re-dissolved, and the solution then again precipitated with sulphuretted hydrogen, to ensure the complete removal of every trace of zinc from the precipitate (§ 162, A, β).

d. The filtrate is neutralized with ammonia and then precipitated with sulphide of ammonium; the precipitate is treated exactly as directed § 108, *b*; the oxide of zinc obtained, which contains sesquioxide of iron and sesquioxide of manganese, is weighed, and the manganese determined volumetrically in a weighed portion of it (§ 161, 13, *d*, 93); the sesquioxide of iron being then ultimately determined, in the solution obtained in the latter process, by means of solution of permanganate of potassa, after previous reduction by zinc, as directed in § 113, 2. The quantity of the oxide of zinc is estimated by the difference.

e. The fluid filtered from the sulphide of zinc is acidified with hydrochloric acid, boiled for some time, the separated sulphur filtered off, and the lime and magnesia determined in the filtrate as directed § 154, 4 (30).

f. A separate sample is ignited in the bulb-tube described § 36. The loss of weight of the bulb-tube indicates the amount of water + carbonic acid; the increase of weight of the chloride of calcium tube gives the quantity of the water alone; the difference shows the quantity of the carbonic acid. In cases where the pressure of a considerable proportion of protoxide of iron would impair the accuracy of this indirect estimation of the carbonic acid, one of the methods described § 139, II., *e*, may be employed.

B. ZINC BLENDE.

This ore consists of sulphide of zinc, commonly mixed with other metallic sulphides, more especially the sulphides of lead, cadmium, copper, iron, and manganese. Besides these, regard must be had in the analysis to the gangue.

The ore is reduced to a very fine powder, which is dried at 212° F.

a. If the ore contains no lead, the *sulphur* in it is determined as directed § 148, II., 1; or, more commonly, as directed § 148, II., 2, *a*, *α* or *β*;—if the ore contains lead, it is treated as directed § 148, II., 2, *b*.

b. The determination of the *metals* should always be made in a separate portion of the pulverized ore. If no lead is present, the powder is dissolved in hydrochloric acid, with addition of nitric acid, and the solution treated as directed § 244, A. In presence of lead, the following convenient method, which gives accurate results, may be resorted to. Heat the powder with fuming hydrochloric acid until complete decomposition is effected, evaporate the fluid to the consistence of syrup, and dilute with 5 or 6 times its volume of strong alcohol. Let the mixture stand several hours; then collect the chloride of lead, together with the undissolved gangue, on a weighed filter; wash with alcohol, dry, and weigh; treat with boiling water until the chloride of lead is completely removed; dry and weigh the residue: the loss of weight suffered in the last operation gives the quantity of the chloride of lead. Free the filtrate from the alcohol, by distillation or evaporation, and proceed with the hydrochloric acid solution as directed § 244, A.

VOLUMETRICAL DETERMINATION OF ZINC.

§ 245.

Several methods have been proposed for the volumetrical determination of zinc; some of them are expeditious, but not very accurate; others give pretty accurate results, but are by no means simple and expeditious. They are less suitable for accurate analyses than for technical purposes. Some of them require the zinc in solution as ammonio-oxide, others as acetate. I will first describe the preparation of these solutions, and then proceed to give a description of the methods.

a. Preparation of Ammoniacal Solution of Zinc.

Treat the zinc ore with warm nitrohydrochloric acid until the soluble part is completely dissolved, and if silicate of oxide of zinc is present, remove the silicic acid by evaporating to dryness and treating the residue with hydrochloric acid. Mix the unfiltered acid solution with ammonia to neutralize the free acid, then add a sufficient excess of a mixture of 3 parts of solution of ammonia with 1 part of solution of carbonate of ammonia. Heat gently for some time in a porcelain dish, filter, and wash the precipitate with ammoniated water. If the zinc ore contains manganese, add to the acid solution of zinc solution of soda until the free acid is just neutralized, then hypochlorite of soda, to precipitate the manganese, heat gently with an excess of pure ammonia and carbonate of ammonia, and proceed as above. There is a trifling error inherent in the preparation of the ammoniacal zinc solution, as the precipitate is not quite free from oxide of zinc, particularly if there is a somewhat large proportion of iron present.*

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* As regards the direct treatment of roasted zinc ores with a mixture of ammonia and carbonate of ammonia, I refer to *E. Schmidt's* paper on the subject, in "Journ. f. prakt.

b. Preparation of Solution of Acetate of Zinc.

Treat the ore with nitrohydrochloric acid as in *a*, drive off the greater part of the free acid, nearly neutralize with carbonate of soda, add acetate of soda in excess, boil, filter, and wash with boiling water mixed with a little acetate of soda. The solution is free from iron ; it contains the whole of the zinc, but, in presence of manganese, also the whole of the latter metal (§ 160, 8).

1. *H. Schwarz's Method.*[*]

Heat the ammoniacal zinc solution very gently, and mix with a moderate excess of sulphide of ammonium. Allow the precipitated sulphide of zinc to subside, then filter, using a tolerably large plaited filter of good filtering paper, moistened with boiling water, and warming the fluid to accelerate the operation, which would otherwise require considerable time. Wash the precipitate with warm water mixed with a little ammonia, until the last drops no longer impart a black tint to a solution of oxide of lead in solution of soda.

Transfer the filter with the precipitate to a beaker, add a dilute, slightly acidified solution of sesquichloride of iron, cover with a close-fitting glass plate, and let the mixture stand for 10 minutes ; then heat gently. If the process is conducted in this manner, no notable trace of sulphuretted hydrogen escapes, and the sulphide of zinc decomposes completely with the sesquichloride of iron to chloride of zinc, protochloride of iron, and sulphur : $Fe_2Cl_3 + ZnS = ZnCl + S + 2FeCl$.

Now add sulphuric acid, and heat gently until the sulphur has agglutinated into a ball. Filter, wash the filter, and determine the iron in the protochloride in the fluid by solution of permanganate of potassa (§ 112, 2). 2 equivalents of iron correspond to 1 equivalent of zinc. If the quantity of sulphide of zinc is not very great, the filter may be perforated, and the sulphide of zinc washed into a flask which already contains the solution of sesquichloride of iron. The results are satisfactory.

2. *Schaffner's Method* ("Journ. f. prakt. Chem.," 73, 410).

The process requires a solution of sulphide of sodium of known strength. To determine this, dissolve 4 grammes of pure zinc in hydrochloric acid, and dilute the fluid to the volume of 1 litre. 50 cc. of this solution contains 0·2 grm. of zinc.

Introduce 50 cc. of this solution into a flask holding about 600 cc., with a mark cut into the glass at the point up to which it holds 300 cc. ; add a mixture of 3 parts of solution of ammonia and 1 part of solution of carbonate of ammonia in sufficient excess to redissolve the precipitate formed ; then add water up to the mark, mix by shaking, and add

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Chem.," 51, 257. By this treatment, the oxide of zinc, which was combined with carbonic acid is dissolved, whilst the greater part of the oxide, combined with silicic acid, remains undissolved.

[*] See *H. Schwarz's* "Anleitung zu Maassanalysen," Suppl. p. 29 (Brunswick). Compare also *v. Gellhorn* ("Chem. Centralbl.," 1853, 291), who has made many analyses of zinc ore by *Schwarz's* method.

4 drops of a tolerably concentrated solution of sesquichloride of iron. Thick flakes of hydrated sesquioxide of iron form, which collect at the bottom of the flask. Now add, from a burette with compression clamp, slowly and gradually, solution of sulphide of sodium, imparting at the same time a gentle swinging motion to the fluid in the flask, but without shaking, as it is of importance to keep the larger portion of the flakes of hydrated sesquioxide of iron at the bottom. A white precipitate of sulphide of zinc forms, and the lighter flakes of hydrated sesquioxide of iron rising towards the surface and coming thus into contact with the solution of sulphide of sodium, gradually acquire a black color, which imparts a grayish tint to the precipitated sulphide of zinc. The flakes at the bottom, however, still remain yellow, which shows that there is as yet no excess of sulphide of sodium. Should no dense yellow flakes remain visible at the bottom of the flask at this stage of the process, add again two drops of solution of sesquichoride of iron. Now add slowly, drop by drop, some more solution of sulphide of sodium, always allowing a certain time to pass before every fresh addition, since the action of sulphide of sodium upon hydrated sesquioxide of iron is not instantaneous; continue this operation until the blackening of the flakes of hydrated sesquioxide of iron at the bottom shows that the whole of the zinc is precipitated, and that the mixture contains a certain excess of sulphide of sodium. Note now the volume of the solution of sulphide of sodium in the burette. If a small portion of the fluid is filtered, and the filtrate mixed with solution of zinc, the faint white turbidity produced will, in some measure, indicate the excess of sulphide of sodium. Empty the flask, then introduce into it some of the ammoniacal mixture, add water up to the mark, then 4 drops of solution of sesquichloride of iron (and, if required, afterwards 2 drops more); add solution of sulphide of sodium from the burette until the yellow flakes have turned black. Deduct the quantity of solution of sulphide of sodium used to produce this effect from the volume consumed in the first experiment; the difference indicates the quantity required to precipitate 0·2 grm. of zinc. Repeat the entire process several times, and take the mean of the results, which, notwithstanding the greatest care in operating, will never quite agree (compare Analytical Notes and Experiments, No. 100). The graduated solution of sulphide of sodium keeps pretty well in securely stoppered bottles, properly protected from sun and heat; however, the safer course always is to determine the strength of the solution before every fresh series of experiments, made after a certain lapse of time.

Now take of the ammoniacal solution of the zinc ore, a quantity containing approximately 0·2 grm. of zinc, transfer to the above described flask, dilute up to the mark, mix with solution of sesquichloride of iron, and treat with solution of sulphide of sodium, exactly as above directed. The strength of the solution of sulphide of sodium being known, the quantity of zinc contained in the examined fluid is found by a simple calculation.

The results, though not very accurate, are still sufficiently so for industrial purposes, provided the dilution of the zinc solution and the other conditions given be pretty nearly the same as here described; but if this is not the case, the results are very inaccurate.

Barreswil ("Journ. de Pharm.," 1857, 431; "Polyt. Centralbl.," 1858, 285) has proposed to introduce into the fluid small pieces of thoroughly ignited porcelain, moistened with solution of sesquichloride of iron, instead of adding 4 or 6 drops of the latter. I have tried this modification, but with less satisfactory results than the original method. It has also been proposed to heat the fluid to boiling; I cannot recommend this, as some sulphide of ammonium will invariably escape from the boiling fluid.

If the operator does not mind a little trouble, the exact point at which the precipitation of the sulphide of zinc is completely effected, and the sulphide of sodium just begins to be present in excess, may be determined with greater precision than by the blackening of the flakes of hydrated sesquioxide of iron, by the following course of proceeding: Moisten a piece of white filter paper with solution of acetate of lead, lay it on a few sheets of blotting paper, let a few drops of carbonate of ammonia fall on it, so that a thin film of carbonate of lead forms on the moderately moist paper; when the excess of moisture has been absorbed by the blotting paper, spread the lead paper on a porcelain plate. As soon as there is reason to suppose that the zinc is nearly precipitated, place a small piece of filtering paper on the lead paper, and transfer a drop of the fluid from the flask to the filtering paper, by means of a blunt glass rod, with moderate pressing. The appearance of a brown spot on the paper indicates that the fluid contains a trifling excess of sulphide of sodium. I consider this lead paper still more sensitive than the otherwise equally useful paper moistened with nitroprusside of sodium, recommended for the same purpose by *Carl Mohr* (Dingler's "Polyt. Journ.," 148, 115). The results obtained with the aid of these papers are more accurate than by *Schaffner's* original process, but the experiment occupies more time. The dilution of the zinc solution and the other conditions given must be pretty nearly the same as described in the process.*

3. *Carl Mohr's Method* (Dingler's "Polyt. Journ." 148, 115).

This ingenious method is based upon the following reactions:—

I. If a solution of acetate of zinc, acidified with acetic acid, is mixed with an excess of ferricyanide of potassium, the whole of the zinc is thrown down in form of a reddish yellow precipitate of ferricyanide of zinc $3\ Zn\ (Cy_6\ Fe_2)$.

II. If solution of iodide of potassium is now added in excess, 2 equivalents of ferricyanide of zinc decompose with 2 equivalents of iodide of potassium, forming 3 equivalents of ferrocyanide of zinc, 2 equivalents of acetate of potassa, 1 equivalent of hydroferrocyanic acid, and 2 equivalents of free iodine: $2\ [3\ Zn\ (Cy_6\ Fe_2)] + 2\ K\ I + 2\ (\overline{A}, HO) = 3\ [2\ Zn\ (Cy_3\ Fe),] + 2\ KO,\overline{A} + 2\ H\ (Cy_3\ Fe) + 2\ I.$

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* *C. Mohr* (Dingler's "Polyt. Journ.," 148, 115) proposes, in presence of manganese, to add tartrated alkali to the ammoniacal solution of zinc. Although this addition will serve to prevent the precipitation of sulphide of manganese from a pure ammoniacal solution of protoxide of manganese, I cannot recommend the proceeding, as the sulphide of zinc precipitated by sulphide of sodium from an ammoniacal solution of zinc containing manganese, will, even in presence of a large proportion of tartrated alkali, always contain sulphide of manganese.

III. 1 equivalent of liberated iodine corresponds, accordingly, to 3 equivalents of zinc.

IV. If iodide of potassium is made to act upon ferricyanide of zinc in neutral solution, the liberated iodine acts upon the ferrocyanide of potassium present in that case, which leads to the formation of a little ferricyanide of potassium; the remaining free iodine, therefore, will not indicate, under these circumstances, with any degree of accuracy, the quantity of zinc present. Whereas, if the reaction takes place in an acid solution of acetate of zinc, prepared as directed in *b*, it may be assumed that acetate of potassa and free hydroferrocyanic acid are formed; and as iodine exercises no appreciable action upon the latter substance, the iodine liberated in the process indicates, with tolerable accuracy, the amount of zinc present.

The process is as follows:—

Mix the acid solution of acetate of zinc, prepared according to the directions of *b*, with ferricyanide of potassium in slight excess—viz., until a sample of the clear supernatant fluid gives a blue precipitate with a salt of protoxide of iron. Then add a sufficient quantity of iodide of potassium. The fluid acquires a brown color, in consequence of the liberation of iodine; the white precipitate of ferrocyanide of zinc is suspended in the brown fluid.

Determine now the free iodine by means of hyposulphite of soda § 146, 3), and calculate 3 equivalents of zinc for each equivalent of iodine. The results obtained by *C. Mohr*, and also in my laboratory, are very satisfactory. The method can be employed only if the acetic acid solution contains no other heavy metal besides zinc, and, more particularly, no manganese.

15. Analysis of Cast Iron.

§ 246.

Cast iron, one of the most important productions of metallurgic industry, contains a whole series of elements, mixed in greater or less proportion with the iron, or combined with it. Although the influence which the various foreign substances mixed with the iron exercise on the quality of cast iron is not yet accurately known, still the fact that they do exercise considerable influence on the quality of the article is beyond doubt. The analysis of cast iron is one of the more difficult operations of analytical chemistry. The following bodies must be had regard to in the analysis:—

Iron, *carbon* (combined with the iron), carbon in form of *graphite*, *silicon*, *phosphorus*, *sulphur*, potassium, sodium, calcium, magnesium, aluminium, chromium, titanium, zinc, *manganese*, cobalt, nickel, *copper*, tin, arsenic, antimony, vanadium. As a general rule, the elements in italics alone are quantitatively determined.

1. Determination of the Carbon.

a. Determination of the total amount of Carbon present.

Of the many methods proposed for effecting the determination of the total amount of carbon present in cast iron, two deserve special mention.

In one of these, proposed by *Berzelius*, the iron is treated with a solution of chloride of copper, and the undissolved carbon converted, by combustion, into carbonic acid, and weighed in that form; in the other the pulverized iron is subjected at once to the combustion process of organic analysis.

α. *Berzelius's* method, slightly modified. Treat about 5 grammes of the cast iron, moderately comminuted, with a concentrated solution of chloride of copper, as free as possible from acid, and let the mixture stand at the common temperature. As soon as the part remaining undissolved presents a mixed mass of copper and separated carbon, &c., crumbling under pressure, add hydrochloric acid, and, if necessary, some more chloride of copper, and digest until the whole of the copper is dissolved to subchloride. Filter through a tube of the form shown in Fig. 146, the narrow part of which is loosely stopped with spongy platinum or thoroughly ignited asbestos. Wash well, dry thoroughly, and treat the entire contents of the tube, either as directed § 177, or as directed § 179. After emptying the tube, rinse with a little chromate of lead or oxide of copper; if the combustion is to be effected in a little boat, in a current of oxygen gas, rinse with oxide of mercury.

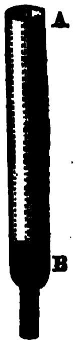

Fig. 146.

β. If the cast iron is to be subjected at once to the combustion process of organic analysis, it must first be reduced to a fine powder. The harder sorts are broken on the anvil, stamped in a steel mortar (§ 25, fig. 21), and passed through a tin wire sieve with very small meshes; the softer sorts are filed with a well-tempered file. Samples of cast iron which cannot be reduced to powder by these means, must be treated by some other method.

Regnault, who was the first to employ this method, and *Bromeis* ("Annal. d. Chem. u. Pharm.," 43, 242) use a mixture of chromate of lead with chlorate of potassa in the process of combustion. *Kudernatsch* ("Journ. f. prakt. Chem.," 40, 499), who observed that the use of these agents is attended with a slight evolution of chlorine, prefers oxide of copper. *H. Rose* recommends oxide of copper and ignition in a current of oxygen gas (§ 179 *a*); *Wöhler* uses the method described § 179, *b* (combustion in a small boat, in a current of oxygen gas); *Mayer* recommends the use of chromate of lead mixed with bichromate of potassa (§ 177). Although the water need not be determined, it is always advisable to place a chloride of calcium tube between the combustion tube and the potassa apparatus, to absorb the moisture.

b. Determination of the Graphite.

Treat another portion of the sample with moderately concentrated hydrochloric acid, at a gentle heat, until no more gas is evolved; filter the solution as in *a*, *a*, wash the undissolved residue, first with boiling water, then with solution of potassa, after this with alcohol, and lastly with ether (*Max Buchner*, "Journ. f. prakt. Chem.," 72, 364); then dry, and burn as in *a*, *a* (§ 177 or § 179). Direct weighing is not advisable, as the graphite generally contains silicon. Deduct the graphite obtained in *b* from the total amount of carbon found in *a*; the difference gives the combined carbon.

2. Treat 50 grammes of the cast iron, coarsely pounded, with a

mixture of 1 part of pure strong nitric acid, and 2 parts of pure strong hydrochloric acid,* until the soluble part is completely dissolved.

Dilute with water, and filter, through a weighed filter, into a litre flask. Wash the residue well, dry at 212° F., and keep in a well-closed tube, for subsequent examination (see 2 *b*). Dilute the filtrate to the volume of 1000 cc., and mix thoroughly by shaking.

a. Examination of the Solution.

a. Heat 200 cc. of the solution, corresponding to 10 grammes of the sample of cast iron, with bisulphite of soda until the sesquioxide of iron is reduced; then heat gently until the fluid smells no longer, or barely, of sulphurous acid; conduct sulphuretted hydrogen into it, and let the mixture stand for 24 hours; then filter from the precipitate formed, and separate the metals which the latter may contain (*arsenic, antimony, tin, copper*), by the appropriate methods described in Section V. Boil the filtrate for some time, to expel every trace of sulphuretted hydrogen; add a little sesquichloride of iron, then carbonate of soda until the free acid is nearly neutralized, and, lastly, carbonate of baryta. Close the flask, let the precipitate, which must have a reddish-white color, deposit, and filter after 12 hours. The precipitate contains the silicic acid and phosphoric acid of the nitrohydrochloric acid solution, combined with sesquioxide of iron. Dissolve in hydrochloric acid, separate the *silicic acid* by evaporating to dryness, and determine the *phosphoric acid* in the filtrate by molybdate of ammonia (§ 134, I., *b*, *β*). In the statement of the results of the analysis, the phosphoric acid is entered as phosphorus; the silicic acid may originally have been present partly in that form as slag, partly in form of silicon. It should be tested for titanic acid (see *β*).

β. Saturate 200 cc. of the nitro-hydrochloric acid solution nearly with carbonate of soda, add acetate of soda, and boil, &c. (§ 161, 2).

aa. Well wash and dry the *precipitate*, ignite, reduce in a current of hydrogen gas (§ 160, 3, *a*), and extract the iron with very dilute nitric acid. Ignite and weigh the residue, which consists chiefly of silicic acid and alumina, and may also contain titanic acid. Evaporate the weighed residue with hydrofluoric acid, to remove the silicic acid; fuse with bisulphate of potassa, dissolve in water, and boil the solution for a considerable time, which will throw down the *titanic acid*, if any is present (§ 107); lastly, precipitate the *alumina* by ammonia or sulphide of ammonium. As the alumina precipitate may contain phosphoric acid, treat it, without previous weighing, as directed § 135, *f*, *β*, taking care to add a little chlorate of potassa to the silicic acid and carbonate of soda used in the process. Should *sesquioxide of chromium* have been present with the alumina, the solution will, besides phosphoric acid, also contain chromic acid. Dilute the nitric acid solution of the iron to a definite volume, boil a suitable portion of it, and precipitate the *iron*, in form of sesquioxide, by ammonia.

bb. Saturate the solution with sulphuretted hydrogen, add ammonia to alkaline reaction, then a little yellow sulphide of ammonium, close the flask, and let it stand for 12 hours. If a precipitate forms, treat this by the appropriate methods described in Section V. It generally contains *manganese*, sometimes *cobalt*, *nickel*, and *zinc*. If the filtrate contains *lime* and *magnesia*, separate these earths also by the proper method given in Section V.

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* To test the acids for sulphuric acid, nearly evaporate to dryness, dissolve the residue in water, and test the solution with chloride of barium.

γ. Add chlorine water to another portion of 200 cc., then precipitate with ammonia and some carbonate of ammonia, filter, evaporate to dryness, and gently ignite the residue, to expel the chloride of ammonium; then separate the magnesia from the *potassa* and *soda* which may be present, as directed § 153, 4, *a*, δ (**18**).

δ. Evaporate another portion of 200 cc. to a syrupy consistence, dilute largely with water, add chloride of barium, and allow the fluid to stand for 24 hours. Wash the precipitated sulphate of baryta thoroughly, dry, and weigh. If washing should fail to free the precipitate completely from all extraneous matter, determine the sulphuric acid in it as directed § 132, II., *b*, *a*.

b. Examination of the Residue insoluble in Nitro-Hydrochloric Acid.

Fuse a portion with carbonate and nitrate of soda, boil the fused mass with water, and subject both the solution and the residue to a careful qualitative analysis. The graphite and charcoal are consumed in this operation; the silicic acid passes into the alkaline solution; besides silicic acid, there may be present also a little phosphoric acid, sulphuric acid, arsenic acid, and chromic acid, as arsenide, phosphide, chromide, &c., of iron are decomposed by acids with some difficulty. As a general rule, however, it will only be necessary to determine the silicic acid as directed § 140, II., *a*.

The residue occasionally contains *titanic acid*; the best way of detecting this, is first to burn the charcoal and graphite, then to volatilize the silicic acid by treating with hydrofluoric acid, to fuse the residue with bisulphate of potassa, to treat the fused mass with cold water, and to boil the clear solution for a considerable time (§ 107).

3. Should the iron exceptionally contain *Vanadium*, the method proposed by *Sefström* may be employed ("Pogg. Annal.," 21, 47; *Rose's* "Handbuch d. Annal. Chem.," II., 764.)

4. The arrangement of the results of the analysis is made upon the assumption that the bodies found were present in the elementary form. However, if the iron was mixed with slag, the component parts of the latter, and, more particularly, therefore, the silicon must not be treated in this manner. It is difficult to decide in what form the silicon found was originally present in the analysed iron, as it may have been present, *a*, as crystallized silicon, similar to graphite; *b*, as silicide of iron; *c*, as silicic acid in the slag. The following is, in my opinion, the best way to settle the question:—Treat the cast iron with chloride of copper free from acid, until the iron is completely dissolved; filter and wash the residue; the filtrate may contain part of the silicic acid formed from the silicide of iron; this may be easily determined as directed § 140, II., *a*. Digest the residue with sesquichloride of iron, out of contact of air, to dissolve the precipitated copper, and wash the undissolved portion, which contains a matter resembling humus, and, in the case of gray cast iron, graphite, and perhaps, besides, crystallized silicon, slag, oxide of silicon,

and hydrated silicic acid formed from this, carbide of iron, phosphide and arsenide of iron, chromide and vanadide of iron, molybdenum, &c. (*Wöhler*). Filter, dry at 212° F., weigh, and subject a portion of the dried and weighed residue to an accurate qualitative analysis. To determine now the silicon in the several forms in which it is present in the analysed iron, proceed as follows :—Treat a portion of the residue, for a short time, with a moderately strong solution of potassa, which will dissolve oxide of silicon and hydrated silicic acid ; remove these from the solution in form of silicic acid. Ignite the washed residue, with access of air, to ensure the combustion of the graphite and charcoal, and heat the incombustible part, which is assumed to consist of slag and crystallized silicon, in a dry current of chlorine, free from air ; the silicon volatilizes as chloride of silicon. The silicic acid of the slag is found by the difference. Deduct the silicic acid of the slag, together with the bases combined with the same (alumina, lime, &c.,)* from the component elements of the analysed cast iron.

SUPPLEMENT TO II.

QUANTITATIVE ESTIMATION OF GRAPE SUGAR AND FRUIT SUGAR, CANE SUGAR, MILK SUGAR, STARCH, AND DEXTRINE.

The quantitative estimation of these compounds is often called for in the analysis of agricultural and technical products and pharmaceutical preparations ; it is also of some importance in the examination of diabetic urine. I will therefore give in this supplement some of the best methods of effecting it.

Setting aside the purely physical processes, which are based either upon the specific gravity of the saccharine solutions, or upon their deportment with polarized light,† there are principally two methods by which the quantitative estimation of grape sugar may be accomplished, and also that of the other compounds, which are convertible into grape sugar.

A. METHOD BASED UPON THE REDUCTION OF OXIDE OF COPPER TO SUBOXIDE.‡

§ 247.

If a solution containing sulphate of copper, neutral tartrate of potassa, and solution of soda, *in the proper proportions*, is heated, even to full ebullition, it remains unaltered ; but if the same solution is heated after addition of grape sugar, suboxide of copper separates. The quantity of the oxide of copper reduced is proportional to the quantity added of the grape sugar : 1 equivalent of the latter ($C_{12}H_{12}O_{12}$) = 180 reduces 10 equivalents of oxide of copper = 396·8 to the state of suboxide (*Fehling*,

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* Supposing, of course, these latter can be determined by analysis of the slag accompanying the sample of cast iron sent for examination.

† Interesting papers on the optical method have recently been published by *Listing* ("Annal. d. Chem. u. Pharm.," 96, 93), and *Pohl* ("Chem. Centralbl.," 1857, 11. *Brix* ("Chem. Centralbl.," 1855, 267) has given new tables on the relation between the specific gravity of the saccharine compounds and the proportion of saccharine matter severally contained in them.

‡ Compare *Fehling*, On the Quantitative Estimation of Sugar and Starch by Means of Sulphate of Copper, "Ann. d. Chem. u. Pharmacie," vol. 72, p. 106 ; and *C. Neubauer*, "Archiv der Pharmacie," 2 series, vol. 72, p. 278.

C. Neubauer). Therefore, if we know the quantity of oxide of copper reduced, we know also that of grape sugar added.

Upon this principle two methods may be based. Either we may add to a solution of copper of known strength, the exact quantity of grape sugar required to reduce all the oxide to suboxide; or the solution of copper may be used in excess, and the suboxide which separates determined. The former method is the one most frequently employed; the latter is resorted to in cases in which, from the dark color of the fluid, it is difficult to determine the exact point at which the process of reduction and separation is accomplished.

We will now proceed, first to the quantitative estimation of grape sugar, and afterwards to the consideration of the best method of converting cane sugar, starch, &c., into grape sugar.

1. Quantitative Estimation of Grape Sugar in pure or almost pure Aqueous Solution.

First Method.

Requisites.

a. Solution of Copper.—Dissolve exactly 34·632 grammes of pure crystallized sulphate of copper, completely freed from adhering moisture by pulverizing and pressing between sheets of blotting paper, in about 200 c.c. of water. Dissolve in another vessel 173 grammes of perfectly pure crystallized tartrate of soda and potassa in 480 c.c. of pure solution of soda of 1·14 sp. gr. Add the first solution gradually to the second, and dilute the deep blue clear fluid exactly to 1000 c.c. Every 10 c.c. of this solution contain 0·34632 grm. of sulphate of copper, and correspond exactly to 0·050 grm. of anhydrous grape sugar. Keep the solution in a cool, dark place, in well-stoppered bottles, filled to the top, as absorption of carbonic acid would lead to the separation of suboxide of copper upon mere exposure to heat; this might be prevented, however, by a fresh addition of solution of soda. Before using the solution, boil 10 c.c. of it for some minutes, by way of trial, with 40 c.c. of water, or dilute solution of soda if there is reason to believe that the fluid has absorbed carbonic acid; if this operation produces the least change in the fluid and causes the separation of even the smallest quantity of suboxide, the solution is unfit for use.

b. Solution of Sugar.—This must be highly dilute, containing only $\frac{1}{2}$, or, at the most, 1 per cent. of sugar. If, therefore, you find, in a first experiment, that the sugar solution is too concentrated, dilute it with a definite quantity of water, and repeat the experiment.

The Process.

Pour 10 c.c. of the copper solution into a porcelain dish, add 40 c.c. of water, or very dilute solution of soda if required; heat to gentle ebullition, and allow the sugar solution to drop slowly and gradually into the fluid, from a burette or pipette divided into $\frac{1}{10}$ c.c. After the addition of the first few drops, the fluid shows a greenish-brown tint, owing to the suboxide and hydrated suboxide suspended in the blue solution; in proportion as more of the sugar solution is added, the precipitate becomes more copious, acquires a redder tint, and subsides more speedily. When the precipitate presents a deep red color, remove the lamp, allow the precipitate to subside a little, and give to the dish an inclined position, which will enable you readily to detect the least bluish-green tint. To make quite sure, however, pour a small portion of the clear supernatant fluid into a test-tube, add a drop of the sugar solution, and apply heat. If there remains the least trace of salt of copper undecomposed, a yellowish-red precipitate will form, appearing at first like a cloud in the fluid. In that case, pour the contents of the test-tube into the dish, and continue adding the solution of sugar until the reaction is complete. The original amount used of the solution of sugar contains 0·050 grammes of anhydrous grape sugar.

When the operation is terminated, ascertain whether it has fully succeeded, that is, whether the solution really contains neither copper, sugar, nor a brown product of the decomposition of the latter substance. To this end filter off a portion of the fluid while still quite hot. The filtrate must be colorless (without the least brownish tinge). Heat a portion of it with a drop of the copper solution; acidify two other portions, and test the one with ferrocyanide of potassium, the other with sulphuretted hydrogen: neither of these tests must produce the slightest alteration. If the fluid contains a perceptible quantity either of oxide of copper or of sugar, this is a proof that too little or too much of the latter has been added, and the experiment must accordingly be repeated.

The results are constant and very satisfactory. Bear in mind that the solution of sulphate of copper must always remain strongly alkaline; should the sugar solution be acid, some more solution of soda must be added.

Second Method.

This requires the same solutions as the first. Pour 20 c.c. of the solution of copper and 80 c.c. of water, or of highly dilute solution of soda if required, (or a larger quantity of the copper solution diluted with water or solution of soda in the same proportion,) into a porcelain dish; add a measured quantity of the dilute sugar solution, but not sufficient to reduce the whole of the oxide of copper, and heat for about 10 minutes on the water-bath. When the reduction is completed, wash the precipitated suboxide of copper by decantation with boiling water. Pass the decanted fluid through a weighed filter, dried at 212° F., then transfer the precipitate also to the filter, dry at 212° F., and weigh. Or determine the quantity of the suboxide by *Schwarz's* method (§ 119, 4, *a*); or ignite the suboxide of copper, with access of air, and then convert it completely into oxide by treating with fuming nitric acid.

100 parts of anhydrous grape sugar correspond to 220·5 of oxide of copper,* or 198·2 of suboxide of copper,† or 155·55 of iron, converted from the state of sesquichloride to that of protochloride.

In the application of this method, it must be borne in mind that the separated suboxide of copper will, upon cooling of the supernatant fluid, gradually redissolve to oxide, being reconverted into this by the oxygen of the atmosphere. Hence the necessity of washing the precipitate by decantation with boiling water.

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* *Fehling* ("Annal. d. Chem. und Pharm.," vol. 72, p. 106) obtained, as highest result, 219·4 grammes of oxide of copper.

† *Neubauer* ("Archiv. der Pharm.," 2 series, vol. 72, p. 278) found in his experiments with starch, that 0·05 of the latter correspond to 0·112 of suboxide of copper. As 90 of starch give 100 of grape sugar, 0·05 of the former correspond to 0·0555 of the latter. Accordingly 100 of grape sugar gave actually 201·62 of suboxide of copper, instead of 198·2.

2. Modification of the Preceding Methods, and Conversion of Cane Sugar, Starch, &c., into Grape Sugar.

a. The preceding methods may be employed without modification to determine the amount of grape sugar contained in *grape juice, apple juice, and the juices of other fruits*, properly diluted of course. The same applies also to *diabetic urine*. The other substances contained in the said juices, and in urine, are generally without perceptible action or influence upon the test solution of copper. However, if there is reason to apprehend such action, the fluid under examination is mixed, in a measuring flask, with acetate of lead, until the foreign matters are precipitated; water is then added to the mark, the mixture allowed to deposit, filtered through a dry filter, and the filtrate examined as directed in 1 (*Fehling*).

b. Vegetable juices of dark color must previously be clarified; this is done by heating a measured quantity of the juice just to boiling, and adding a few drops of milk of lime, which usually produces a copious precipitate (of albumen, coloring matter, lime salts, &c.); the fluid is then filtered through animal charcoal, the precipitate thoroughly washed, and the washings added to the filtrate, which is then diluted to 10, 15, or 20 times its original bulk (*Neubauer*).

c. Cane sugar, or vegetable juices containing cane sugar (the juices of the sugar cane, beetroot, maple, &c.), must first be converted into grape sugar. This is effected by protracted heating with dilute sulphuric acid. Thus, for instance, to prepare beetroot juice for the quantitative estimation of the saccharine matter contained in it, take 15—20 c.c. of the juice treated as directed in *b*, add 12 drops of dilute sulphuric acid (SO_3,HO + 5 water), and boil the mixture from 1 to 2 hours, adding water as it evaporates; this operation is conducted best in a steam-bath. Neutralize the free acid by means of a dilute solution of carbonate of soda, dilute to 10 or 20 times the original volume, and examine the fluid as directed in 1.

100 parts of grape sugar ($C_{12}H_{12}O_{12}$) correspond to 95 parts of cane sugar ($C_{12}H_{11}O_{11}$). Accordingly, it takes 0·0475 grm. of cane sugar to decompose 10 c.c. of the copper solution.

d. Starch and *dextrine*, or substances containing either of these bodies, are treated in the same way, but the action of the sulphuric acid is continued much longer than in the conversion of cane sugar into grape sugar. For instance, to convert 1 gramme of starch into grape sugar, proceed as follows: mix the gramme of starch with 10 grammes of cold water, shake the mixture, apply heat, still shaking, until a paste is formed; add to this 12 drops of dilute sulphuric acid (1—5), and apply heat until the fluid becomes thin; boil now from 6 to 10 hours in an obliquely placed flask on the sand-bath, frequently replacing the evaporated water;[*] or heat the fluid from 24 to 36 hours in the steam-bath. When the conversion into grape sugar is completed, dilute the fluid to 100 or 200 c.c., and proceed as directed in 1. The reaction with tincture of iodine, which has been proposed by several chemists as a test to ascertain whether the conversion into grape sugar is completed, is not sufficiently reliable. To remove all doubt on the subject, heat 20 c.c. of the fluid again for 3 hours, with a few drops of dilute sulphuric acid, rinse into a measuring tube, dilute to 40 c.c., and proceed again as directed in 1. This second experiment must take exactly double the quantity of solution of copper used in the first; if less is required, this is a proof that an additional quantity of sugar has been formed upon the renewed application of heat.*

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[*] The operation may be greatly facilitated by closing the flask with a perforated cork furnished with a glass tube bent at an obtuse angle, and which leads to a condensing apparatus turned upwards; by this arrangement the evaporated water is returned to the flask.

100 parts of grape sugar ($C_{12}H_{12}O_{12}$) correspond to 90 parts of starch ($C_{12}H_{10}O_{10}$); or 10 c.c. of the copper solution correspond to 0·045 of starch.

e. *Milk sugar* reduces a much smaller proportion of oxide of copper than grape sugar; for whilst 1 equivalent of the latter decomposes 10 equivalents of oxide of copper, 1 equivalent of milk sugar reduces only 7 or 8 equivalents. Milk sugar, must, therefore, before the application of the test, first be converted into grape sugar, by boiling its solution for 1 hour with a little sulphuric acid.

To determine the milk sugar in milk, the caseine is removed by means of acetic acid, and the whey cleared with a little white of egg and filtered; the filtrate is boiled with a little sulphuric acid, then mixed with 9 times its volume of water, and the sugar determined in the usual way, as directed in 1.

B. METHOD BASED UPON THE DECOMPOSITION OF SUGAR BY ALCOHOLIC FERMENTATION.†

§ 248.

1. When a saccharine fluid is exposed, with ferment, or yeast, to the proper temperature, it suffers alcoholic fermentation, in which the elements of 1 equivalent of anhydrous grape sugar are converted into 2 equivalents of alcohol and 4 equivalents of carbonic acid ($C_{12}H_{12}O_{12}) = 2 (C_4H_6O_2) + 4 C O_2$. Accordingly, if the quantity of carbonic acid generated in this way is known, the quantity of sugar decomposed may be calculated from it. 100 parts of anhydrous grape sugar give 51·11 of alcohol and 48·89 of carbonic acid. This calculation is not quite correct, however, as in the fermentation of sugar some other products are also formed (amylic alcohol, butylic alcohol, &c.) The method, therefore, cannot pretend to absolute accuracy.

2. The carbonic acid escaping in the process is most conveniently determined with the aid of the flask A of the apparatus, illustrated in Fig. 66 (§ 139, II., *e*, *a*, *aa*). To prevent receding, the flask B is replaced by a U-shaped tube, containing pumice-stone saturated with sulphuric acid; the quantity of sulphuric acid must be just sufficient to fill up the bend of the tube. The outer limb of the U tube is closed by a cork, with a very narrow glass tube, open at both ends, fitted into it.

3. The experiment is made with a quantity of the saccharine fluid containing about 2 or 3 grammes of anhydrous sugar. If much more is taken, the fermentation lasts too long; if, on the other hand, much less is used, the results are inaccurate, because the quantity of the carbonic acid evolved is in that case too small for correct weighing.

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* The complete conversion of starch into sugar may be effected also by making the starch into paste, and digesting this for several hours, at a temperature of from 140° to 158° F., with a measured quantity of infusion of malt. If the sugar is now determined in an equal quantity of infusion of malt, heated for the same time, the difference gives the amount of sugar formed from the starch.

† Compare *Krocker*, on the quantitative estimation of starch in various cereals, "Annal. der Chem. und Pharm.," vol. 58, p. 212.

4. As regards the concentration of the fluid, the solution should contain about 4 or 5 parts of water to 1 part of sugar. More highly dilute solutions must therefore be concentrated by evaporation on the water-bath.

5. Pour the sugar solution into the flask A, add a few drops of solution of tartaric acid, and a comparatively large weighed portion of washed yeast (say 20 grammes of fresh, or a corresponding quantity of German yeast). As yeast generally evolves some carbonic acid from its own constituents, a larger weighed portion of it may be put into another similar apparatus, to determine the carbonic acid evolved from it, which is then calculated for 20 grammes, *i. e.* the quantity used in the fermentation process of the sugar, and the resulting amount deducted from the weight of the carbonic acid obtained in the latter.

6. The apparatus is now accurately weighed, and kept at a pretty constant temperature of 77° F. Fermentation soon sets in, and goes on briskly at first, but after a time more slowly. When no more gas bubbles escape through the sulphuric acid (after 4 or 5 days), the process is terminated. The flask A is now heated by placing it in a vessel with hot water; it is then taken out of the bath, and the carbonic acid still lingering in the apparatus sucked out by means of a caoutchouc tube; the apparatus is then allowed to cool, and after this re-weighed. The loss of weight indicates the amount of carbonic acid which has escaped, and this multiplied by 2·045 gives the corresponding quantity of grape sugar.

7. If it is intended to examine amylaceous substances in this way, the starch in them is converted into grape sugar in the manner directed § 247, 2, *d*; the fluid is then evaporated in the water-bath to the consistence of syrup, transferred to the flask A, and the free sulphuric acid removed, by adding a highly concentrated solution of neutral tartrate of potassa in sufficient quantity to form sulphate and bitartrate of potassa;* the fluid is then subjected to the process of fermentation. In the examination of potatoes, 6—8 grammes are used; in that of the different sorts of flour of the cereals, 3 grammes.

III. ANALYSIS OF THE ASHES OF PLANTS.†

§ 249.

The recent researches and discoveries of agricultural chemistry have fully established the fact, that plants require for their growth and development certain inorganic constituents, which are different for the different classes of plants; the discovery of this fact has created a very natural desire to ascertain *which* inorganic constituents are respectively indispensable for the growth of the several species of plants, and more particularly for that of the cultivated plants, and also for weeds, since the knowledge of the constituents of these latter enables us to infer the nature of the soil in which they grow. This knowledge it was endeavored to attain by the analysis of the ashes remaining upon the combustion of either the entire plants or particular parts of them (the seeds for instance). And, although it is a settled point that perfectly accurate results cannot be so obtained, since the ashes of a plant do not quite truly represent the sum of the inorganic constituents contained in it, still, putting aside a few experiments made in this direction,[†] we know as yet no better means of obtaining the end in view, and at all events no other means equally applicable to the analysis of all vegetable matters. The analysis of the ashes of plants will therefore continue, at least for some time to come, a highly important and interesting branch of analytical chemistry; nay, we may safely presume that this mode of estimating the inorganic constituents of plants will never be abandoned by the agriculturist, since the results which it gives are sufficiently accurate for the purposes of agriculture, though not for those of physiology.

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* The reaction on litmus paper affords a tolerably safe guide as to the quantity required.

† As the analysis of the ashes of animal substances is made almost exclusively for scientific, and only rarely for technical purposes, I have omitted in the text a detailed description of it; I will here only remark, that the same processes which are given in the text for the incineration of plants and the analysis of the ashes will equally serve for animal substances. Substances which fuse are first heated, according to *H. Rose*, in a platinum dish, with stirring, until they have lost their fluidity, and the organic matter is nearly destroyed. The nearly charred residue is transferred to a platinum or common clay crucible; the lid is securely closed, and the contents are heated to dull redness. The charcoal obtained is burnt with spongy platinum. *Strecker's* method of incineration, which is given in the text, is also well adapted for animal substances. According to

The ashes of plants containing, according to the researches hitherto made, only a limited number of acids and bases, certain widely applicable methods for their analysis have been devised. As these methods present many peculiarities, and are frequently employed, I will here describe those which appear to me the simplest and the best adapted for the purpose. A critical discussion of the numerous and essentially different methods proposed would of course be out of place in the present work.

The following are the substances generally found in plants:—

Bases:

Potassa, soda, lime, magnesia, sesquioxide of iron, proto-sesquioxide of manganese.

Acids and Salt-radicals:

Silicic acid, phosphoric acid, sulphuric acid, carbonic acid, chlorine.

Slater ("Chem. Gaz.," 1855, 53), the most practical way of effecting the incineration of animal substances, is to mix and ignite them with pure, dry, finely pulverized binoxide of barium. In a paper on the subject ("Annal. der Chemie und Pharmacie," 73, 370), *Strecker* calls attention to the fact that the ashes of animal substances often contain no inconsiderable quantity of cyanates. These salts are destroyed most readily by moistening the ashes with water, and then heating gradually to redness; one moistening usually suffices to convert the cyanates into carbonates. On the subject of the analysis of the ash of animal substances, compare also *F. Verdeil's* paper on the analysis of the ash of the blood of man and several animals ("Annal. der Chem. und Pharmacie," 69, 89; "Pharmac. Centralbl.," 1849, 198; *Liebig* and *Kopp's* "Annual Report," 1849, 599); and *Fr. Keller'* paper on the ash of flesh and broth ("Annal. der Chem. und Pharmacie," 70, 91; "Pharm. Centrabl.," 1849, 581; *Liebig* and *Kopp's* "Annual Report," 1849, 599).

[*] *Caillat* states that, by treating grass plants (clover, lucern, sainfoin) with dilute nitric acid, he succeeded in removing the inorganic constituents so fully that the readily combustible residuary mass left, upon incineration, for 10 grammes of vegetable used, only from 18 to 22 milligrammes of ash, consisting of silicic acid and sesquioxide of iron. He states, moreover, that this treatment of the plant gives a larger quantity of the constituents of the ash, more particularly of sulphuric acid, than is obtained by the incineration of the plant. ("Compt. Rend.," xxix. 137; *Liebig* and *Kopp's* "Annual Report, 1849, 601).—*Rivot*, *Beudant* and *Daguin* ("Compt. Rend.," 1853, 835; "Journ. f. Prakt. Chem.," 61, 135) propose to destroy the organic matters by treating with solution of potassa and conducting chlorine into the mixture.

Besides these, we occasionally find alumina (*e.g.*, in the ashes of the lycopodiaceæ, in comparatively large proportion), baryta, fluorine, iodine, bromine, metallic cyanides and cyanates (only in the ashes of bodies abounding in nitrogen), boracic acid, metallic sulphides, and often slight traces of oxide of copper, occasionally also of oxide of zinc, or of other oxides of heavy metals.

Most of these substances were unquestionably originally constituents of the incinerated plants; as regards some others, it is uncertain whether they were originally present in the vegetable, or whether they owe their formation to the process of incineration; and, lastly, some of them, certainly owe their origin entirely to that process. Thus the sulphates and, exceptionally, even the carbonates, may have been original constituents of the plant; but they may also have been formed, in the process of incineration, by the destruction of salts with organic acids, and by the combustion of the sulphur which every plant contains in the unoxidized state; thus the metallic sulphides are formed by the action which the charcoal exercises upon sulphates in the absence of a sufficient supply of air;—thus the metallic cyanides owe their formation to the effect of heat upon nitrogenous charcoal in contact with alkaline carbonates; and the cyanates to the oxidation of the metallic cyanides, &c.

From the variety of these several inorganic substances, and the circumstance that some of them are usually present in very minute quantities only, it is by no means an easy task to devise universally applicable methods; more especially, as it is always a great desideratum to unite accuracy with despatch.

The analysis of the ashes of plants is properly divided into four parts, viz.:—

1. The preparation of the ash;
2. The analysis of the ash;
3. The calculation and statement of the results;
4. The calculation of the per-centage proportion in which the several constituents of the ash are present in the plant or part of a plant which has furnished them.

A. PREPARATION OF THE ASH.

§ 250.

In the preparation of the ash for the analytical process, the following conditions must be had regard to:—

1. The plant or part of a plant to be incinerated, must be free from all adhering impurities.
2. The ash must be as free as possible from unburnt matters.
3. No essential constituents must be lost by the process of incineration.

To satisfy the *first* condition, the plants or parts of plants intended for incineration must be carefully selected and cleaned. It is not always practicable to rub or brush away sand or clay, more especially from small seeds. *H. Rose* gives the following directions for cleaning the latter:—

Pour over the seeds, in a beaker, a moderate quantity of distilled water, stir a few moments with a glass rod, and then place on a sieve with sufficiently wide meshes to allow the fine sand to pass through, whilst retaining the seeds. Repeat this operation several times, but take care never to leave the seeds long in contact with water; otherwise soluble salts might be extracted from them. Finally, place the seeds on a linen cloth, and rub between its folds, which will remove the still adhering fine sand; dry them, to be ready for the process of incineration when required. Seeds cleaned in this manner are almost perfectly free from foreign matters.

For the fulfilment of the *second* and *third* conditions, the principal point to be looked to is that the incineration must be effected at the lowest possible temperature (a dull red heat), and with proper access of air, neither too strong nor too feeble. Too strong a draught is apt to carry away particles of the ash, whilst, on the other hand, with too feeble a draught, the operation lasts too long, and facilities are afforded for processes of reduction. The application of an over-intense heat will cause the fusion of the metallic chlorides and the phosphates of the alkalies, and the fused mass enfolding the carbon will very greatly impede the combustion of the latter; besides, excessive heat may cause the metallic chlorides to volatilize; nay, even phosphoric acid may be lost in this way, since, as *Erdmann* has shown, acid phosphates of the alkalies, when ignited with carbon, are converted into neutral salts, with reduction and volatilization of part of the phosphorus. But, whilst loss of metallic chlorides and phosphoric acid may be effectually guarded against by properly regulating the heat and the access of air, and, if need be, by mixing baryta or lime with the substance intended for incineration, loss of carbonic acid cannot be avoided. The quantitative estimation of the carbonic acid in the ash will, therefore, never enable us to draw any reliable inference as to the constituents of the incinerated vegetable. It was formerly thought that the presence of carbonates in the ash of a plant containing no carbonates, might be regarded as a proof of the presence of salts with organic acids in the incinerated plant; however, even this assumption has been shown to rest on error, since alkaline carbonates may easily be formed by the action of alkaline nitrates upon charcoal; and, moreover, as *Strecker* has shown, alkaline carbonates are formed, together with alkaline pyrophosphates, when tribasic alkaline phosphates are ignited with a large excess of sugar, or the charcoal of the latter. On the other hand, alkaline pyrophosphates are converted into tribasic phosphates when strongly ignited in conjunction with alkaline carbonates. With these facts before us, we can readily understand how the detection and estimation of tribasic and bibasic phosphates in an ash may also depend upon the manner of incineration.

But least of all will the quantitative estimation of the sulphuric acid in the ash of a plant enable us to judge of the constituents present, even if the incineration is effected with addition of an alkaline earth. For plants contain, in the first place, sulphuric acid in form of sulphates, and, in the second place, sulphur in organic combinations, especially in the albumen. A correct process of incineration will, indeed, give the whole of the sulphates present; but most certainly, in many cases, increased by other sulphates formed in the process. This much, however, is positive, that the quantity of sulphuric acid found in the ash of a plant will never serve to determine, even approximately, the amount of sulphur contained in the plant.*

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* Comp. *Mayer*, "Annal. d. Chem. u. Pharm.," 101, pp. 136 and 154.

I will now proceed to describe the several methods of incineration.

1. *Incineration in the Muffle.*

This method, which was first recommended by *Erdmann*,* and afterwards by *Strecker*,† and which is at present introduced in most laboratories, has almost entirely superseded the old way of burning vegetable substances in hessian crucibles placed in an oblique position.

The muffles which I employ are made of the material of hessian crucibles; they are in internal measurement 28 centimetres long, 11 centimetres wide, and 6 centimetres high. They are placed in furnaces with movable grates; they have no conducting pipe, and are loosely closed in front with a perforated door. The circulation of air thus created is quite sufficient for the combustion of the charred substance.

a. The substance which it is intended to incinerate (about 100 grammes) is dried at 212° or 230° F. Succulent roots and fleshy roots are cut in slices and laid on glass plates. The dried substance is weighed, and then put into a shallow platinum or porcelain capsule, or, better still, into a shallow platinum or porcelain dish, fitting exactly in the muffle; the dish or capsule is introduced into the latter, which is then gradually heated. When the evolution of empyreumatic products ceases, the heat is a little increased, but not beyond a very faint redness not visible in daylight. At this temperature, which is not sufficiently high to fuse either chloride of sodium or pyrophosphate of soda, the carbon burns with feeble incandescence, and 12 hours suffice to produce a quantity of ash free from carbon, sufficient for the purposes of analysis. Substances to which this mode of incineration is unsuited, are charred first, at a gentle red heat, in a large covered platinum or hessian crucible, and the charred mass is subsequently incinerated in the muffle. As a general rule, the operator had always better refrain from stirring the mass in progress of incineration, since this would tend to diminish the porosity. According to *Strecker*, no chloride of sodium volatilizes in this process of incineration.

The ash obtained is weighed, reduced to powder, properly mixed, and kept in a well-stoppered bottle.

b. Vegetable substances leaving upon incineration an ash abounding in alkali salts, more particularly in chloride of the alkalies, which are, accordingly, readily fusible, are generally charred in a crucible at the lowest possible temperature, then treated with water until the principal portion of the soluble salts is extracted, the residue dried, and finally incinerated in the muffle. The ash is weighed, and the aqueous solution of the soluble part diluted to the exact point to give just as many tenth, half, or whole cubic centimetres of fluid as there are milligrammes of ash of the insoluble portion. For the analytical process the weighed quantities of the ash are then severally mixed with a corresponding number of cubic centimetres of the solution. I have employed this method with great success in the analysis of marigold (see "Journ. f. prakt. Chem.," 70, 85). To ascertain the total amount of the ash, a measured portion of the solution is evaporated to dryness, weighed, the part calculated upon the whole, and the result (representing the residue which the entire solution would leave upon evaporation) added to the weight of the ash of the insoluble portion.

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* "Ann. d. Chem. und Pharm.," 54, 353.

† Ibid., 73, 366.

2. *Incineration in the Dish, with the aid of an Artificial Current of Air* (*F. Schulze*).*

Char the organic substance, properly dried at 212° F., and weighed, in a platinum or hessian crucible, at a gentle red heat, and transfer the charred mass to a shallow platinum dish; put a triangle of platinum wire across the dish, and place on the triangle a common lamp chimney,† which may be secured in position, if desirable, by means of a retort holder. Heat over gas or over a spirit lamp. The increased current of air caused by the chimney, and which may be regulated by taking a longer or shorter one, and placing it higher or lower, suffices to effect the complete incineration, even of the cereal grains, at the temperature of the spirit-lamp.‡ When the incineration is completed, weigh the ash, and proceed as in 1.

3. *Incineration with the aid of an Artificial Current of Air* (*Hlasiwetz*, "Ann. d. Chem. u. Pharm.," 97, 244).

This method requires a silver, platinum, or porcelain tube of the form of a tobacco pipe. For difficultly combustible charcoal it should be cylindrical, 7 inches long, 1¼ inch wide, and with the lower end tapering to a point. A platinum plate with 6—8 small perforations prevents charcoal or ashes falling out. For readily combustible charcoal a conical or crucible-like shape is given to the tube. It is fitted air-tight into one tubulature of a two-necked *Woulf's* bottle, which is connected in the usual way with a second and third, and the latter with a very large aspirator (a barrel). The second bottle and the third are not quite half filled with water. If water is made to flow from the barrel by opening the cock, air rushes in through the tube, and passes through the water in the second and third bottles. The process is conducted as follows:—Char the properly comminuted organic substance in a porcelain crucible with the lid on. As soon as the gases cease to burn, project the feebly incandescent charcoal through a funnel into the tube, and at once open the cock of the aspirato a little. Regulate the cock so as to ensure the proper combustion of the charcoal at a moderate temperature. Stir the mass occasionally together into a heap by means of a platinum wire. Heat the ash finally for a short time in a platinum dish, to ensure the combustion of the last remaining particles of charcoal. In the water of the *Woulf's* bottles traces of fixed salts are found, more particularly of metallic chlorides; also carbonic acid and ammonia. If the fixed salts are present iu ponderable quantity, they must be determined.

4. *Incineration in the Muffle, with addition of Baryta* (*Strecker*, "Annal. der Chem. und Pharm.," 73, 366).

Dry the organic substance at 212° F., and char it slightly, in a porcelain or platinum dish, over the lamp. Moisten the charred mass with a concentrated solution of *pure* hydrate of baryta in sufficient quantity to leave, after the incineration of the mass, a mixture of about equal parts by weight of ash and baryta. Dry the moistened mass again, and then burn it in the muffle at the lowest possible temperature. The ash is kept from fusion by the baryta; it remains bulky and loose, and thus permits a complete combustion of the carbon.

The residue must still contain a considerable excess of carbonate of baryta. If this is not the case, there is reason to apprehend a loss of sulphur or phosphorus, and it is therefore in that case advisable to incinerate a fresh portion of the vegetable substance with a larger addition of baryta than has been used with the first portion.

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* Communicated to me by letter.

† Instead of a chimney, a sufficiently wide neck of a retort may be used.

‡ *F. Schulze* employs this method also for the incineration of filters; he places the crucible with the filter in the dish.

Reduce the incinerated residue to a fine powder, mix this intimately, and keep it in a well-stoppered bottle.

5. *Incineration with the aid of Spongy Platinum* (*H. Rose*).

Char about 100 grammes of the substance dried at 212°, in a platinum or clay crucible, at a dull red heat; reduce the charred mass to a fine powder by trituration in a porcelain mortar; mix the powder most intimately with 20—30 grammes of spongy platinum; transfer the mixture in portions to a shallow thin platinum dish, and heat over gas or over a lamp with double draught. After a short time, and before the mixture is in a state of ignition, every particle of carbon begins to glimmer, and a gray layer speedily covers the surface of the black mixture. By diligent and cautious stirring with a little platinum spatula, the surface is renewed and the combustion promoted. As long as the mass contains unconsumed carbon, glimmering is observed; but when the carbon is entirely burnt, all visible incandescence ceases, even though a stronger heat be applied. When the incineration is completed, mix the mass uniformly, dry thoroughly, and weigh. Deduct from the weight that of the platinum added; the difference expresses the weight of the ash.

B. Analysis of the Ash.

§ 251.

Before proceeding to the description of the analytical process, I have to remark that, of the methods of incineration described in the preceding paragraph, those *sub* 1 and 2, and more particularly *b*, when properly executed, fully answer the purpose in most cases.

I have deemed this observation necessary to explain why the analytical process which I am now on the point of describing refers exclusively to ashes prepared by the method 1 or 2 (or 3), which accordingly contain no extraneous admixture of baryta or platinum. The modifications which this process may require in cases where the incineration of the vegetable substance has been effected by method 4 or 5, are only trifling, and such as will readily suggest themselves.

According to their principal constituents, the ashes of plants may be classed under the following heads:—

a. Ashes in which *carbonates of the alkalies and alkaline earths* predominate; *e.g.*, the ashes of woods, of herbaceous plants, &c.

b. Ashes in which *phosphates of the alkalies and alkaline earths* predominate; to this class belong the ashes of nearly all kinds of seeds.

c. Ashes in which *silicic acid* predominates; *e.g.*, those of the stalks of the gramineæ, of the equisetaceæ, &c.

Although it is quite obvious that the limits between the different classes cannot be drawn very strictly, this classification must yet be maintained, in order to impart a certain degree of clearness and simplicity to the analytical methods which I am now going to describe; for the general process requires of course certain modifications according to the class to which the ashes under examination belong.

a. Qualitative Analysis.

As the constituents are known which are usually found in the ashes fluous. A few preliminary experiments suffice to ascertain the presence or absence of the more rarely occurring constituents, and also, more particularly, to fix the class to which the ash under examination belongs. These experiments are as follows :—

1. *The ash under examination is heated with concentrated hydrochloric acid, to see whether it is completely decomposed thereby or not.* If the ash strongly effervesces when the acid is poured over it, this may be taken as a proof of its decomposition by that agent. The ashes of the stalks of gramineæ, &c., which abound in silicic acid, are usually the only kind that resists complete decomposition by hydrochloric acid.

2. If the hydrochloric acid solution of an ash is, after separation of the silicic acid and removal of the greater part of the free acid, mixed with an alkaline acetate, or neutralized with ammonia and free acetic acid added, a gelatinous yellowish-white precipitate of phosphate of sesquioxide of iron will almost invariably separate. Now, it is necessary to ascertain *whether the ash contains any phosphoric acid besides that in this precipitate.* For this purpose the fluid is filtered from the precipitate, and ammonia in excess added to the filtrate; if this *fails to produce* a precipitate, or if the precipitate formed is red, and consists accordingly of hydrated sesquioxide of iron, this is a proof that the ash contains no more phosphoric acid; but if, on the contrary, a white precipitate is formed (phosphate of lime and phosphate of magnesia and ammonia), this is a positive proof that the ash contains more phosphoric acid than is combined with the sesquioxide of iron present, and must consequently be classed under the second head.

3. *The ash is tested for manganese,* by mixing a small portion with carbonate of soda, and exposing the mixture on platinum foil to the outer flame of the blowpipe (compare *Fresenius*' "Qualitative Analysis").

4. The ash is tested for alumina, baryta, iodine, bromine, fluorine, and other occasional constituents of vegetable ashes, if it is desirable to ascertain whether traces of them are present (compare *Fresenius*' "Qualitative Analysis").

b. Quantitative Analysis.

I. *Ashes in which the Carbonates of the Alkalies or Alkaline Earths predominate, and in which the whole of the Phosphoric Acid may be assumed to be combined with Sesquioxide of Iron.*

§ 252.

The ash is divided into two portions, which we will call A and B.

In B we determine the carbonic acid[*] and the chlorine.

In A the remaining constituents.

A. 1. DETERMINATION OF THE SILICIC ACID, CHARCOAL, AND SAND.

Introduce 4 or 5 grammes of the ash into a porcelain dish, and add dilute hydrochloric acid. If the ash abounds in carbonates, cover the loss from spurting is effectively guarded against. As soon as the carbonic acid has been completely expelled, rinse the funnels into the dish; then apply a gentle heat until no more undecomposed ash is visible, with the exception of the carbonaceous and sandy particles which are almost invariably present, and may be readily distinguished. Evaporate now to dryness on the water-bath with frequent stirring in the last stage of the process, until all the lumps are reduced to powder.

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[*] The estimation of the carbonic acid, though, as we have seen above, of no great value in itself, is yet necessary to complete the analysis, and thus to supply a certain control.

Moisten the dry mass, after cooling, with concentrated hydrochloric acid, and let this act for about 30 minutes; then add a proper quantity of water, and heat to incipient ebullition; pass the acid fluid afterwards through a weighed stout filter, dried at 212° F.

The silicic acid remains upon the filter, mixed with charcoal and sand, if the ash contains these substances. The mass upon the filter is thoroughly washed, carefully dried, and subsequently transferred from the filter to a platinum dish, without injuring the filter. If the powder is perfectly dry, this may be readily accomplished, only a few particles of charcoal remaining attached to the paper, just sufficient to color it slightly. The powder is now boiled for half an hour with a dilute solution of pure soda (free from silicic acid), or with a concentrated solution of carbonate of soda, which gradually effects the total solution of the silicic acid without affecting the sand or charcoal that may be present. The fluid is passed through the same filter as before, and the undissolved residue thoroughly washed and then dried with the filter at 212° F., until the weight remains constant. The weight of the filter is deducted from that of the residue, which is entered in the calculation of the results as *charcoal* and *sand*.

The filtrate is supersaturated with hydrochloric acid, and the *silicic acid* in it determined as directed § 140, II., *a*.

2. DETERMINATION OF ALL THE REMAINING CONSTITUENTS, WITH THE EXCEPTION OF CHLORINE AND CARBONIC ACID.

The hydrochloric acid solution filtered from the undissolved silicic acid, charcoal, and sand, is most intimately mixed with the rinsing water; the fluid is then divided, by weight or measure, into three, or, better still, four parts, since this will leave one part for unforeseen accidents. The best way of effecting the division, is to filter the fluid into a measuring flask holding 200 c.c., to fill up to the mark with the washing water and with pure water, and shake; to measure off with a pipette three equal portions of 50 c.c. each (the fourth portion being kept in the flask). We will designate these three portions severally, *a*, *b*, and *c*.

In *a*, we determine phosphate of sesquioxide of iron, and the alkaline earths, and also the free sesquioxide of iron and the manganese which may be present.

In *b*, the sulphuric acid.

In *c*, the alkalies.

a. Determination of the Phosphate of Sesquioxide of Iron, &c., and of the Alkaline Earths.

Mix the fluid with ammonia until a permanent precipitate is formed, add acetate of ammonia and a sufficient quantity of free acetic acid to impart a distinct acid reaction to the fluid; application of a gentle the precipitate, wash the latter with hot water, dry, ignite, and weigh. Calculate as Fe_2O_3, PO_5[*] (compare § 93, 4, *d*).

Saturate the filtrate with ammonia and determine the *lime* and *magnesia* as directed § 154, 4, *a* (30).

However, should a precipitate of hydrate of sesquioxide of iron form upon addition of ammonia to the filtrate, this precipitate must first be filtered off and determined; and should the filtrate contain an appreciable quantity of manganese, either alone or with iron, this must, after saturating the fluid with ammonia, first be removed by precipitation with sulphide of ammonium before the estimation of the alkaline earths can be effected. The precipitated sulphide of manganese, if pure, is treated according to § 109, *c*; if containing iron, according to § 160.

b. Determination of the Sulphuric Acid.

Precipitate the fluid *b* with chloride of barium, and determine the precipitate as directed § 132, 1.

c. Determination of the Alkalies.

Mix the fluid *c* with a quantity of chloride of barium just sufficient to precipitate the sulphuric acid, as estimated in *b*, and evaporate on the water-bath until the greater part of the free acid is removed; then add pure milk of lime in slight excess, and heat for some time on the water-bath; filter. This process serves to remove the whole of the sulphuric acid, phosphoric acid, sesquioxide of iron, and magnesia. Wash the precipitate until the last washings produce no longer the least turbidity in solution of nitrate of silver; remove the excess of lime from the filtrate by means of carbonate of ammonia mixed with ammonia; let the precipitate subside, and filter the fluid; evaporate the filtrate to dryness in a platinum dish, and ignite the residue; redissolve and precipitate again and, if necessary, a third time, with ammonia and carbonate of ammonia.[†] Evaporate the last filtrate to dryness, ignite the residual alkaline chlorides gently, weigh, and separate the *soda* and *potassa* (if both alkalies are present) as directed § 152.

N.B. If the quantity of ash is small, the fluid filtered from the silicic acid may also be divided into only two parts, instead of three, and the sulphuric acid and alkalies determined in one, by first precipitating the sulphuric acid by the least excess of chloride of barium, and then proceeding according to the directions of *c*.

B. DETERMINATION OF THE CARBONIC ACID AND CHLORINE.

Determine the carbonic acid in another portion of the ash, as directed § 139, II., *e*, *a*, *bb*. Filter the contents of the flask, and precipitate the chlorine with solution of nitrate of silver, as directed § 141, I., *a*.

N.B. If the quantity of ash is very small, the whole of the constituents may also be determined in one and the same portion. In this case, the carbonic acid is first determined as in B, the fluid passed through a weighed filter, the chlorine determined in the filtrate, and the excess of filtrate; the further process is conducted as in A. The rinsed filter is dried, and the residual charcoal, sand, and silicic acid are subsequently again collected on it.

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[*] Should the precipitate contain phosphate of alumina, or should any doubt be entertained regarding its composition, the weighed precipitate must be examined as directed § 135.

[†] In fact, until the solution of the gently ignited residue is no longer rendered turbid by ammonia and carbonate of ammonia.

II. *Ashes decomposed by Hydrochloric Acid, which contain Phosphoric Acid also in other forms of combination than with Sesquioxide of Iron.*

§ 253.

Take two portions of the ash, a larger, A, and a smaller, B. Determine in B, the carbonic acid and chlorine as in § 252; in A, the other constituents. If the quantity of ash is very small, determine the whole of the constituents in one and the same portion (see § 252, B, N.B.).

Treat A with hydrochloric acid, and separate the silicic acid, charcoal, and sand as in § 252. Dilute the hydrochloric acid solution to the volume of 150 c.c., and divide this into two parts, one of 50 c.c. (*a*), the other of 100 c.c. (*b*).

Determine in *a* first the *sulphuric acid*, by adding chloride of barium in the least excess; then add solution of sesquichloride of iron until the fluid appears yellow, remove the greater portion of the free acid by evaporation on the water-bath, dilute, and mix the fluid, after cooling, cautiously with carbonate of baryta in proper excess (the precipitate must be of a light reddish-brown color). After a few hours, filter, remove the lime and baryta from the filtrate by carbonate of ammonia and a little oxalate of ammonia, then separate the magnesia, together with the last remaining traces of baryta, by oxalic acid, as directed § 153, 4, δ (18); determine the *alkalies* as chlorides, and separate them, if required, according to the directions of § 152. If the solution contains an appreciable quantity of *manganese*, precipitate this first, after the removal of the phosphoric acid, with sulphide of ammonium.

Mix *b* with ammonia in slight excess, then add acetic acid until the precipitated phosphates of the alkaline earths are redissolved. Filter the *phosphate of sesquioxide of iron*, which remains undissolved, and treat as in § 252, 2, *a*. Divide the filtrate into two equal parts, α and β, and determine in α the *phosphoric acid* as phosphate of sesquioxide of uranium, as directed § 134, *c*; in β the *lime* and *magnesia* as directed § 154, 4, *b* (31). If the ash contains an appreciable quantity of manganese, the latter must be removed from the portion intended for the estimation of the lime and magnesia (β), as that metal will otherwise precipitate partly with the lime, partly with the magnesia. In that case, therefore, heat β (which still contains alkaline acetate, the fluid having been mixed with acetic acid) to 122°—140° F., and transmit chlorine through it (§ 159, B, 4, *a*, β [58]).

The fluid *b* may also be treated as follows:—Proceed first as above directed; after the separation of the phosphate of sesquioxide of iron, precipitate the lime from the acetic acid solution by oxalate of ammonia (§ 103, 2, *b*, β). Filter, divide the filtrate into two equal parts, and determine the magnesia in one, by addition of ammonia and phosphate of soda; the phosphoric acid in the other, by addition of ammonia and solution of sulphate of magnesia mixed with chloride of ammonium.

In presence of an appreciable quantity of manganese, this latter method gives less satisfactory results. If the phosphoric acid is present in the dish, fuse the residue with carbonate of soda, dissolve the fused mass in water, and determine the phosphoric acid in the solution either as phosphate of sesquioxide of uranium, or by addition of ammonia and solution of sulphate of magnesia mixed with chloride of ammonium.

III. *Ashes not decomposed by Hydrochloric Acid.*

§ 254.

The carbonic acid, which, however, is rarely found in ashes of this class, is determined according to the directions of § 252. The same applies to chlorine. The estimation of the other constituents requires a preliminary decomposition of the ash; this may be effected in several ways, as follows:—

1. Evaporate the ash with pure solution of soda to dryness, in a platinum or silver dish. (The results of many experiments have shown that by this operation the silicates in the ash are completely decomposed, whilst the sand which may be mixed with the ash is left untouched, or, at least, nearly so. The heat must not be raised in the last stage of the process sufficiently high to fuse the mass.) Pour dilute hydrochloric acid over the residue, evaporate, treat again with hydrochloric acid, and proceed with the insoluble residue (silica, charcoal, and sand), as directed in § 252, A, 1; with the solution as directed in § 252, A, 2, or 3. The alkalies cannot, of course, be determined in the solution; they are estimated in a separate portion of the ash, which for this purpose is decomposed either by hydrofluoric acid, or by fusion with hydrate of baryta (*Fresenius* and *Will*).

2. *Way* and *Ogston* * mix the ash with an equal weight of nitrate of baryta, and fuse the mixture gradually in a large platinum crucible (transferring it to the crucible in small portions at a time). By this process the ash is fully prepared for decomposition by hydrochloric acid, and the charcoal which it may contain is completely destroyed, leaving the ash perfectly white. The silicic acid is separated according to the direction given in § 252, A, 1, and the sulphate of baryta which may be present determined. Of the hydrochloric acid solution, *Way* and *Ogston* use a portion for the estimation of the alkalies, by the method described in § 252, A, 2, *c.*; they precipitate the remainder with sulphuric acid, added slightly in excess;† they then divide the filtrate into two portions, and determine in one the phosphate of sesquioxide of iron, the lime and magnesia (§ 253); in the other the phosphoric acid, as directed § 134, *d*, *β*.

C. CALCULATION AND ARRANGEMENT OF THE RESULTS.

§ 255.

It is only recently that chemists have begun to turn their attention seriously to the analysis of the ashes of plants, for the benefit of vegetable

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* "Journal of the Royal Agricultural Society," VIII., Part 1; *Liebig* and *Kopp's* "Annual Report," 1849, 600.

† As the quantity of nitrate of baryta used is known, an excess over the calculated weight of sulphate of baryta shows that lime has been thrown down with the baryta: the quantity of this sulphate of lime is calculated from the excess of the weight of the precipitate.

1. Do plants absolutely require certain quantities of certain constituents? and if so, *what* are these constituents?

2. May some of these inorganic constituents be replaced by others?

It is quite obvious that a proper and perfectly satisfactory solution of these questions can be expected only from the results of an exceedingly large number of analyses, and that a great many chemists must contribute towards such a solution.

Under these circumstances, it is of the utmost importance that the results of all analyses of vegetable ashes should be invariably arranged and reported in a uniform manner, so that they may be compared readily and without recalculation.

As the manner in which the bases and acids found were originally combined in the plant cannot be inferred from the ash with any degree of certainty, and since, moreover. as I have already had occasion to state, the ashes differ as regards the phosphates, &c., according to the degree of heat employed,—it is unquestionably the most judicious way to enumerate the per-centage weights of the bases and acids separately. The chlorine, however, is put down as chloride of sodium, and, should the quantity of soda present be insufficient, as chloride of potassium, the proportion of sodium contained in the chloride is calculated as soda, and the calculated weight subtracted from the total amount of soda found; since, otherwise, a surplus would be invariably obtained in the analysis, as the chloride of sodium originally present in the ash would be reckoned as chlorine and *soda*, instead of chlorine and *sodium*. The manganese which may be present is entered as proto-sesquioxide, since it exists in that form in the ash. A mere report of the quantities of the several constituents found in the analysis of an ash, will not afford the requisite data for an accurate comparison of the results with those of other analyses, as it includes, or may include, certain substances which are altogether foreign to the purpose for which the ash is analysed, more especially charcoal and sand. To render practicable a comparison of the results severally obtained in different analyses, these unessential and accidental admixtures (charcoal and sand) must be struck out, and the remaining constituents of the ash calculated in per-centage parts.

A report intended to show the composition of an ash as revealed by the analytical process, must include the carbonic acid among the essential constituents; but if the object of the analysis is to ascertain what are the inorganic salts which a plant derives from the soil, the carbonic acid must be struck out of the calculation, as well as the charcoal and sand.

To satisfy every requirement, it is best to state the results both ways, *i.e.*, inclusive and exclusive of the unessential parts; the first statement will enable chemists to judge of the degree of accuracy of the analysis, the other will facilitate comparisons. If the carbonic acid is omitted from the second report, for the reason stated, the quantity of carbonic acid contained in 100 parts of the ash must be mentioned instead.

CONSTITUENTS OF THE ASH BEAR IN THE COMPOSITION OF THE PLANT, OR PART OF A PLANT, WHICH HAS FURNISHED IT.

§ 256.

The usual way formerly was to incinerate, with proper caution, a small weighed portion of the carefully dried vegetable substance, and determine the total amount of the ash; and then to incinerate a larger unweighed portion, less carefully dried, and analyse the ash obtained. A simple calculation then sufficed to find the per-centage proportions of the several constituents. For instance, some grains of wheat had left upon incineration 3 per cent. of ash, containing 50 per cent. of phosphoric acid : 100 parts of these grains of wheat were therefore assumed to contain 1·5 per cent. of phosphoric acid, &c.

This method is unquestionably most convenient; but, unfortunately, it does not give sufficiently accurate results in all cases, since, from the causes stated in § 250, the total amount of the ash is by no means constant, but varies more or less, within certain limits, according to the manner, intensity, and duration of the process of ignition. As we can, therefore, in most cases, never be sure that the smaller portion obtained in the determination of the total weight of the ash, corresponds exactly in composition, &c., with the larger portion used in the actual analysis, it is always the safer plan to weigh, as I have already recommended in § 250, on the one hand, the total quantity of the (dried) substance intended for incineration, and, on the other hand, the total amount of ash obtained and intended for analysis.

If it is wished to avoid this, the end in view may also be attained in another manner, viz., by incinerating first a large unweighed portion of the vegetable substance, analysing the ash, and determining thus the relative proportions between the several constituents; then incinerating a smaller weighed portion, dried at 212° F., and determining in the ash one of those constituents which are not liable to the least change in quantity from the mode of incineration—*lime*, for instance. As the relative quantity of this substance in the composition of the plant is known, as well as the proportion between it and the other constituents of the ash, it is easy to calculate from these data also the per-centage proportions which the other constituents of the ash bear in the composition of the plant.

IV. ANALYSIS OF SOILS.

§ 257.

THE proposition being fully established that every plant requires for its growth and development certain inorganic matters which are supplied by the soil in which it grows, it is self-evident that the knowledge of the composition of the soil must be a subject of paramount importance to the practical farmer, to enable him, on the one hand, to judge to what kind of plants a given soil will afford the requisite nutriment, and, on the other hand, to adapt a soil for the cultivation of a certain plant by a proper supply of the necessary manure.

was sufficient to know—irrespective of the physical conditions—which of the constituents would dissolve in water, which in dilute acids, and which in neither of these solvents. It was assumed that the substances soluble in water were supplied direct to the plant with the water absorbed from the soil; whilst those soluble in dilute acids were made available by the agency of carbonic acid and salts of ammonia; and the insoluble substances, lastly, were only slowly and gradually prepared, by progressive disintegration and decomposition, to serve as nutriment for plants.

Liebig ("On Modern Agriculture," Letters III. and VIII., Walton and Maberly) has lately refuted this view of the nutrition of plants; he admits, indeed the co-operation of the solvents named, but he attributes to the roots of the plant an inherent faculty of withdrawing and appropriating from the soil substances which neither pure water nor water impregnated with carbonic acid would be able to withdraw. Indeed, arable soil exercises, in a certain sense, a similar action to that of porous charcoal, withdrawing, like the latter, from fluids, substances which they hold in solution, as, *e.g.*, ammonia from ammoniacal solution, silicic acid and potassa from solution of soluble glass, phosphate of ammonia and magnesia from its solution in water impregnated with carbonic acid, &c.; which of course sufficiently proves that these substances cannot be withdrawn from the soil, at least not completely, by water, or water impregnated with carbonic acid.

Now, although the way in which plants take up the inorganic constituents of their food from the soil is not as yet clearly established, this much is certain, that a mere knowledge of the different degrees of solubility of the several constituents will not enable the agricultural chemist to judge of the fertility of a soil; that no useful inferences can be drawn from the component parts of an aqueous extract of the same; and that the state of mechanical division in which the several constituents exist in the soil is of as great importance as the state of solubility.

Besides the inorganic constituents, there are found in most, in fact nearly in all soils, organic substances (vegetable and animal remains and the products of their decomposition). That these organic substances exercise a material influence on the fertility of the soil is unquestionable; and, whatever views may be entertained as to the manner of this influence, this much is certain, that it is highly important to obtain also a knowledge of the nature and quantity of the organic constituents contained in a soil.

The old methods of analysing soils by preparing aqueous extracts, &c., and examining them, are of course no longer applicable; the analytical process is now properly divided into two parts, viz., I., Mechanical Analysis, and, II., Chemical Analysis.

I. MECHANICAL ANALYSIS OF THE SOIL (*Fr. Schulze*, "Journ. f. prakt. Chem., 47, 241).

§ 258.

1. Take samples from different parts of the field, mix intimately, and dry in the air. If the soil contains pebbles or stones, weigh the total quantity of the sample, then pick out the stones and weigh them. Keep the air-dried soil in a wide-mouthed stoppered bottle.

weigh. The loss of weight shows the amount of moisture; calculate this for 100 parts of the dried soil. Suppose, for instance, the air-dried soil is found to consist of 96 parts of dried soil and 4 parts of moisture, 4·17 parts of moisture are calculated for 100 parts. Keep the dried soil for chemical analysis (see II.).

3. Crush the air-dried soil with the hand, if caked, and weigh off a quantity exactly corresponding to 1000 grammes of soil dried at 212° F. Pass this through a wire sieve with meshes 3 millimetres in diameter, fitted on to a bottom for collecting the particles passing through the meshes. As soon as this operation is completed, remove the sieve from the bottom, and place it in a dish (A), pour in water sufficient to cover the contents of the sieve, and wash by hand until the clay is completely separated from the gravel; then rinse the latter thoroughly with water, transfer the contents of the sieve to a dish, dry at 212° F., and weigh. When thoroughly dry, it is then ignited in the air, and the loss of weight indicates the amount of organic matter mixed with the *gravel*.

4. Pass the product of the first sifting through another wire sieve with meshes 0·66 millimetres in diameter, collecting the particles passing through in the bottom, as in the first operation. Remove the sieve, place it in a dish (B), pour in the contents of A, rinse thoroughly with water, adding the rinsings to the contents of B. Wash the earth in the sieve with water until the clay is completely separated from the gravelly sand; then wash the latter thoroughly with water, transfer to a dish, dry at 212° F., and weigh. If the latter is then ignited in the air, the loss of weight indicates the amount of organic matter mixed with the *gravelly sand*.

5. The results of the preceding operations show how much 1000 grammes of earth dried at 212° F. contain of

a. *Gravel*, determined by direct weighing;
b. *Gravelly sand*, „ „
c. {Coarse sand, fine sand, finest particles removable by elutriation,} estimated collectively by the difference, since 1000 grammes —(a + b) = c.

6. To effect the separate determination of each of the component parts of *c*, the soil which has passed through the fine sieve must be elutriated. The apparatus described § 236, A (Mechanical Analysis of Clays), is used for this purpose. Dry about 40 grammes of the product of the second sifting at 212° F., weigh off 30 grammes of the dried soil, transfer to a porcelain dish, add twice or three times the quantity of water, stir, and boil for half an hour. If the soil is very clayey, a porcelain pestle should be used for stirring, instead of a glass rod, and the operation frequently repeated, to ensure the complete separation of the clay from the sand. Transfer the mass after cooling, to the elutriating glass, with proper rinsing, and remove first the clay and fine sand from the coarser sand, then the clay from the fine sand, in the exact manner directed § 236, A (Mechanical Analysis of Clays). The fine sand and the coarse sand are dried at 212° F., weighed, and then ignited with free access of air; the loss of weight severally observed indicates

7. Deduct from the 30 grammes boiled with water, *a* the coarse sand, *b* the fine sand; the difference shows the quantity of the finest particles removed by the process of elutriation, including a certain, though very trifling, proportion of soil dissolved by the elutriating water. Calculate the several quantities of coarse sand, fine sand, and finest elutriated particles found in the 30 grammes, for the total amount of these three constituents found in 1000 grammes of the soil dried at 212° F. (compare *5, c*); and enter the weights found in the report of the results *sub 5, c*; then, by removing the decimal point, convert the per mils, into per cents.

8. The results of the mechanical analysis are properly reported as follows:—

100 parts of the soil dried at 212° F. contain (by way of illustration) say:—

		Fixed substances.	Combustible or volatile substances.
6·90	Gravel, ignited	6·90	
	Organic matter mixed with it . . .		. . 0·00
7·10	Gravelly sand, ignited	6·43	
	Organic matter mixed with it . .		. . 0·67
35·50	Coarse sand, ignited	34·37	
	Organic matter mixed with it . . .		. . 1·13
40·00	Fine sand, ignited	38·50	
	Organic matter mixed with it . . .		. . 1·50
10·50	Finest elutriated particles	9·50	
	Organic matter mixed with it, ammonia salts, and chemically combined water		. . 1·00
100·00		95·70	4·30

2·10 stones in 100 parts of dried soil.

4·17 moisture calculated to have been present in a quantity of air-dried soil, corresponding to 100 parts dried at 212° F.

II. CHEMICAL ANALYSIS.

§ 259.

If the chemical analysis of a soil were pushed to the utmost limit indicated in § 257, it would be necessary to examine each of the component parts separated by the mechanical process, and accordingly to take into consideration also the substances dissolved by the water of elutriation. However, it is generally sufficient for agricultural purposes to confine the analysis to the following processes:—

1. Mix the several samples of soil taken from different parts of the field intimately, dry at 212° F., and heat 100 grammes of the dried soil, with access of air, to feeble ignition (best in a flat vessel of clay, porcelain, or silver, placed in a muffle), until the organic matters are completely destroyed; saturate the residue, after cooling, with a concentrated solution of carbonate of ammonia, dry at a gentle heat, raising the temperature finally to a somewhat higher degree,

tion of weight indicates the *total quantity of the organic substances, ammonia salts, and the chemically combined water*. Pass the ignited residue through the wire sieve with meshes 0·66 millimetres diameter (§ 258, 4), to separate the gravel and gravelly sand from the finer particles (the sand, fine sand, and finest particles of clay). Wash the gravel and the gravelly sand, to remove the still adhering soil, and dry. The coarser and the finer parts so separated are then severally analysed, fractional portions being taken of each, and the results calculated for 100 parts.

2. Weigh off 20 grammes of the gently ignited finer portion of the soil, add water, then hydrochloric acid in moderate excess, heat gently for some time on the water bath, filter* into a half-litre flask, wash until the last washings no longer show an acid reaction, then fill with water to the mark, and mix.

a. Dry the *residue*, ignite gently, weigh, then treat with concentrated sulphuric acid as directed § 236, B, 2nd method, *b*. Should the separated sand be found upon examination to be other than pure quartz sand, another portion of it must be analysed in the way usually employed for silicates.

b. Measure off 4 several portions of the hydrochloric acid *solution*, of 50 or 100 c.c., according to the greater or less proportion of certain constituents present.

In α, determine the *sulphuric acid* as directed § 132, I.

In β, the *phosphoric acid* as directed § 134, *b*, β.

In γ, the *iron* as directed § 113, 2, *a*.†

In δ, the *silicic acid, alumina, protoxide of manganese, lime, magnesia, potassa*, and *soda*. Separate first the silicic acid (§ 140, II., *a*), then the *sesquioxide of iron, alumina, protoxide of manganese, lime, magnesia*, and *alkalies*, by one of the methods given in § 161; if much iron is present, by § 161, 2 (96). Bear in mind that with the sesquioxide of iron and alumina, the whole of the phosphoric acid is also thrown down by acetate of ammonia, and that, therefore, in order to find the alumina, both the sesquioxide of iron found in γ and the phosphoric acid found in β, must be subtracted from the ignited and weighed precipitate.

3. Determine the *carbonic acid* in a separate portion of the gently ignited finer part of the soil, see (1), as directed § 139, II., *e*, *a*, *bb*.

4. Treat portions of the gravel and coarse sand obtained in 1, in the same way as the finer particles in 2 and 3. A further analysis of the part insoluble in hydrochloric acid may often be dispensed with, as the nature of the fragments of stone, &c., can be determined in the mineralogical way.

There remains now still, besides the determination of the organic matter, that of the ammonia, chlorine, and nitric acid. Although it may be assumed that these constituents are present only in the sifted finer unsifted soil.

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* To guard against obstruction of the filter, it is advisable to transfer first the coarser fragments to it, before pouring on the fluid with the mechanically suspended finer particles of clay.

† If the soil contains protoxide of iron, extract a separate portion of the non-ignited finer part with hydrochloric acid, and then determine the protoxide of iron in the solution, as directed § 112, 2, *a*. Calculate this upon the weight of soil contained in γ, and deduct the result from the total quantity of iron found in γ; the difference gives the quantity of iron present as sesquioxide.

5. Boil a tolerably large portion of the air-dried soil (which must be calculated upon soil dried at 212° F.), with dilute milk of lime, best in a small copper still, and determine the expelled *ammonia* by *Boussingault's* method, § 209, 8.

6. To determine the *chlorine*, treat a portion of the soil dried at 212° F. with highly dilute nitric acid in the cold, and precipitate the solution with solution of nitrate of silver (§ 141, *a*).

7. To determine the *nitric acid*, extract a weighed portion of the air-dried soil (which must be calculated upon soil dried at 212° F.), as completely as practicable with water, and treat the extract as directed § 209, 9. Should the presence of larger proportions of organic matters prevent the use of the method described § 149, II., *a*, *α*, the method *β* or *γ*, must be employed.

The aqueous extract may be prepared, either strictly according to the directions of § 214 of *Fresenius's* "Qualitative Analysis," or in the following manner,* which requires the use of a three-necked *Woulf's* bottle, provided also with a lateral tubulated orifice in the lower part. A wide glass cylinder open at the top and narrowing towards the lower end (a percolator), which holds about 1000 grammes of soil, fits air-tight into the middle neck. Push down into the narrow part of the percolator a loose plug of sponge, spread over this a layer of pure sifted gravel, cover the latter with a thick layer of washed fine sand, and then introduce the soil. Fit a tube connected with a hand air-pump into one of the other necks, and close the third neck and the lower opening. Moisten the soil with water, pouring on from time to time a fresh quantity, and continuing in this way for 24 hours; then rarefy the air in the bottle by means of the hand-pump, which will force the water charged with the soluble parts of the soil more rapidly from the percolator into the bottle. When the latter is nearly full, remove the stopper from the third neck, place a vessel under the lower opening to receive the fluid, and then remove the stopper.† The solution so obtained is perfectly clear.

8. *Determination of the Acids of Humus*‡ (*Ulmic, Humic, Geïc Acids*).

Digest from 10 to 100 grammes of the air-dried soil (according as the qualitative analysis has shown the presence of a smaller or greater quantity of the acids of humus) for several hours, at 176°—194° F., with a solution of carbonate of soda; filter. Mix the filtrate with hydrochloric acid to slightly acid reaction; the acids of humus will separate in the form of brown flakes. Collect these flakes on a weighed filter, wash until the water just appears colored; dry, and weigh. Burn the dry mass, deduct the weight of the ash (after subtracting the filter ash) from that of the dry mass, and enter the difference in the calculation as *acids of humus*.

9. *Estimation of the so-called Humus Coal* (*Ulmine* and *Humine*).

Boil a quantity of soil equal to that taken in *e*, in a porcelain dish, water from time to time. Dilute, filter, and wash. Determine the total amount of the acids of humus present in the same manner as in 8. The difference between the weights obtained respectively in 8 and 9, expresses the quantity of humic acid which has been formed from the ulmine or humine by the process of boiling with potassa; enter it in the calculation as *humus coal*.

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* Professor *Fr. Schulze*; communicated by letter.

† If the *Woulf's* bottle is not provided with a lower tubulature, the fluid is removed with the aid of a siphon.

‡ With regard to the estimation of the organic constituents, compare *Otto*, *Sprengel's* "Bodenkunde," page 430, &c.; and also *Fr. Schulze*, "Journ. f. Prakt. Chem.," vol. 47, p. 241, &c.

10. *Determination of the Organic Matter which has not as yet suffered conversion into Humic Acid, Humus Coal, or similar Products.*

Determine the carbon in the soil by the method of organic analysis, either deducting the carbonic acid found in the form of carbonates from the total amount of carbonic acid obtained, or first completely removing the carbonates from the soil by treating with dilute hydrochloric acid and thorough washing,† before proceeding to combustion with oxide of copper. As the oxide of copper need not be very carefully dried, and as the weighing of the chloride of calcium tube is omitted, the process is much simpler than an ordinary organic analysis. According to *Fr. Schulze*, 58 parts of carbon correspond on an average to 100 parts of organic matter in the soil, and 60 parts of carbon to 100 parts of humus substances. The quantity of carbon corresponding to the humus substances is calculated by the latter proportion (60 : 100), the result deducted from the total amount of carbon, and 100 parts of other organic matter are entered for every 58 parts of the difference.‡

11. *Determination of the Nitrogen in a Soil.*

The soil contains, besides the nitrogen of the air enclosed within its pores (which is disregarded), nitrogen in three different forms of combination—viz., ammonia, nitric acid, and organic matter. By determining, by organic analysis, the total quantity of nitrogen contained in a soil, and subtracting from this the nitrogen of the ammonia and nitric acid, we find the quantity of nitrogen present in the organic matter of the soil. The weight of the nitrogen contained in the organic compounds being included already in the results of 10, is not entered in the list as an element of the calculation, but simply by way of information.

12. *Determination of Waxy and Resinous Substances.*

Waxy and resinous substances are found in appreciable quantities in some kinds of soil only. Their determination may be effected in the following manner:—Dry 100 grammes of the soil in the water-bath, boil repeatedly with strong spirit of wine, collect the filtrates in a flask, and distil off half the spirit. Let the mixture cool, which will cause the wax to separate. Collect this on a weighed filter, wash with cold spirit of wine, and determine the weight. Evaporate the filtrate (in the last

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* If the quantity of the humus coal is very considerable, the fluid alone is poured on the filter at first, and the sediment boiled once more with solution of potassa, before it is transferred to the filter.

† The quantity of organic substance dissolved in this process is mostly so trifling that it may safely be disregarded.

‡ If the determination in the bulk of the organic matter present in a soil is deemed sufficient, the chemist may omit the processes 8, 9, and 12, confining the analysis, in this respect, to the estimation of the total amount of carbon, according to the direction of 12, entering 100 parts of organic substance for 59 parts of carbon. To determine the organic matter by the loss of weight which the dried earth suffers by ignition, appears to me altogether inadmissible, as the expulsion of water from the clay, &c., must necessarily render the results quite unreliable.

If the quantity of wax and resin is in any way considerable, it must be deducted from the weight of the acids of humus, as the latter have been weighed inclusive of the waxy and resinous matters.

13. The *results* of the chemical analysis of a soil should be arranged in the manner best calculated to give a correct view of the composition of the soil. I think the following plan best suited for the purpose. The numbers are only given for a few of the constituents, by way of illustration. They are of course arbitrary; but they correspond as far as practicable with those assumed, by way of illustration, in the arrangement of the results of the mechanical analysis.

100 parts of soil dried at 212° F. contain :—

95·70 Fixed substances,	Gravel and gravelly sand, 13·33,	Soluble in hydrochloric acid,	Lime	1·70
			Sesquioxide of iron, Carbonic acid, Phosphoric acid, &c.	
		Insoluble in hydrochloric acid,	Quartz gravel, slate, &c.	7·00
	Finer particles, 82·37.	Soluble in hydrochloric acid,	Lime, Magnesia, Carbonic acid, Phosphoric acid, &c.	
		Decomposed by concentrated sulph. acid,	Alumina, Silicic acid, Potassa, &c.	
		Not decomposed by acids,	Quartz sand.	

		Nitrogen.	Carbon.	
4·30 Combustible or volatile substances, or substances decomposed by ignition,	Ammonia	0·16	...	0·20
	Nitric acid	0·07	...	0·27
	Acids of humus . . .	...	1·20	2·00
	Humus coal . . .	...	0·20	0·33
	Other organic substances	0·05	0·58	1·00
	Chemically combined water and loss	...	...	0·50
100·00		0·28	1·98	100·00

2·10 stones per 100 parts of dried earth.

4·17 moisture per 100 parts of dried soil (air-dried).

To enable the agricultural chemist to pronounce on the quality of a soil, he must, besides the preceding mechanical and chemical analysis, ascertain also the most important physical conditions of the same, such as the actual and the apparent specific gravity, the faculty of retaining water, &c. &c.; and also the power which a soil possesses of withdrawing from aqueous solution certain important elements of the food of plants, more particularly ammonia, dissolved silicic acid, salts of potassa, phosphates, &c. For more detailed information on the subject of the physical condition of soils, I refer to *Schübler*, " Grundsätze der Agripower of a soil may be made by *Liebig's* method, described in "Annal. d. Chem. u. Pharm.," vol. 105, page 113.

V. ANALYSIS OF MANURES.

§ 260.

I **speak** here simply of the manures supplied by the urine and excrements, and the blood and bone of animals. The examination of manures has chiefly a practical object, and demands accordingly simple methods. The value of a manure depends upon the nature and condition of its constituents, of which the following are the most important: organic matters (characterized by their carbon and nitrogen), salts of ammonia, nitrates, phosphates, silicates, sulphates, and chlorides of alkalies or alkaline earths (potassa, soda, lime, magnesia). Respecting the condition in which the ingredients of manures may be deemed to exercise the most effective and favorable action on the soil, our views are much less clear; indeed, it is obvious that a universally applicable and valid rule cannot well be laid down in this respect; since the agriculturist sometimes wishes a manure containing most of its constituents in a state of solution, which will accordingly exercise a speedy fertilizing action,* and sometimes one which will only gradually supply the soil with the substances required by the plants.

I will here give 1, the outlines of a general method of examining manures; 2, methods of analysing guano and bone manures.

A. Analysis of Manures in general.

§ 261.

Mix the manure uniformly by chopping and crumbling, then weigh off successively the several portions required for the various analytical processes.

1. *Determination of the Water.*

Dry 10 grammes in the water-bath, and determine the loss of weight (§ 28). It is rarely necessary to make a correction on account of the carbonate of ammonia which escapes with the water.†

2. *Determination of the total Amount of fixed Constituents.*

Incinerate, at a gentle heat, a weighed portion of the residue left in 1, in a platinum dish (§ 250, 2), or in a large platinum crucible placed in an oblique position, and weigh the ash.

3. *Determination of the Constituents soluble in Water, and also of those insoluble in Water.*

Digest 10 grammes of the fresh manure with 300 c.c. of water, pass of the substances insoluble in water, and the difference—after deducting the water found in 1—gives the amount of the soluble constituents. Incinerate now the insoluble residue, and weigh the ash; the weight of the ash expresses the total amount of the fixed constituents contained in the insoluble part, and the difference between this and the ash in 2 gives the total amount of fixed constituents contained in the soluble part.

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* This sort of manure may, however, prove injurious to tender plants, if applied in too large quantity, without proper dilution with water, and in dry weather.

† The determination of the carbonate of ammonia is best effected by drying the manure in a little boat inserted into a tube; the tube is heated to 212° F., in the water- or air-bath, a current of air being transmitted through it, by means of an aspirator; the air on entering is made to pass through concentrated sulphuric acid, the air passing out through two U-shaped tubes containing standard oxalic acid. After drying, the quantity of ammonia expelled, which has combined with the oxalic acid, is determined (§ 99, 3).

4. *Separate Determination of the several fixed Constituents.*

Dry a larger portion of the manure, and treat it by one of the methods given for the preparation and analysis of the ashes of plants.

5. *Determination of the total amount of Ammonia.*

Treat a weighed portion of the manure by *Schlösing's* method (§ 99, 3, *b*).*

6. *Determination of the total Amount of Nitrogen.*

Moisten a weighed portion of the manure with a dilute solution of oxalic acid in sufficient quantity to impart a feebly acid reaction; dry, and determine the nitrogen, in the entire mass or in a weighed portion, according to the directions given in § 187. Deduct from the total amount of nitrogen so found the quantity corresponding to the ammonia and the nitric acid; the difference shows the quantity of nitrogen contained in the organic substances. It is generally sufficient, however, to know the total amount of the nitrogen.

7. *Determination of the total Amount of Carbon.*

Treat a portion of the dried residue of 1 by the process of organic analysis. If the dried manure contains carbonates, determine the carbonic acid in a separate portion, and deduct the result from the total amount obtained by the organic analysis; the difference shows the quantity of carbonic acid formed in the latter process by the carbon of the organic substances.

8. *Determination of the Nitric Acid.*

Treat a weighed portion of the manure with water, and evaporate the solution, with addition of pure carbonate of soda to distinct alkaline reaction; filter after some time, then evaporate the filtrate to dryness, weigh the residue, and determine in a fractional part of it the nitric acid as directed § 149, II., *a*, α; or, if the presence of organic substances interferes with the application of this method, as directed § 149, II., *a*, β or γ.

B. Analysis of Guano.

§ 262.

Guano, or the dung of sea-fowl, well known for its great fertilizing properties, not only varies very considerably in quality in the different islands from which our supplies are derived, but is often also fraudulently adulterated with soil, brick-dust, carbonate of lime, and other matters. Guano being an important article of commerce, it will be readily understood, therefore, why it should be made the object of chemical examination more frequently than other manures.

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* If the quantity of ammonia is only small, the decimal standard oxalic acid is used.

1. *Determination of the Water.*

This is effected exactly as in § 261, 1. Genuine guano loses from 7 to 18 per cent.

2. *Determination of the total Amount of fixed Constituents.*

Incinerate a weighed portion in a porcelain or platinum crucible placed in a slanting position, and weigh the ash. Good guano leaves from 30 to 33 per cent. of ash, guano of bad quality from 60 to 80 per cent., and a wilfully adulterated article often even more. The ash of genuine guano is white or gray. A yellow or reddish color indicates adulteration with loam, sand, or soil. In the first stage of the process of incineration good guano, in its incipient decomposition by heat, emits a strong ammoniacal odor and white fumes.

3. *Determination of the Constituents soluble in Water, and also of those insoluble in Water.*

Heat 10 grammes of guano with about 200 c.c. of water, pass the solution through a weighed filter, and wash the undissolved portion with hot water, until the water running off looks no longer yellowish and leaves no perceptible residue when evaporated upon platinum foil; dry the residue, and weigh. Deduct the weight of the water and of the insoluble residue from the weight of the guano; the difference expresses the amount of the soluble constituents. Incinerate the insoluble part and weigh the ash; the difference shows the amount of the fixed soluble salts. With very superior sorts of guano, the residue insoluble in water amounts to from 50 to 55 per cent.; with inferior sorts, to from 80 to 90 per cent. The brown-colored aqueous solution of genuine guano evolves ammonia upon evaporation, emits a urinous smell, and leaves a brown saline mass, consisting chiefly of sulphates of soda and potassa, chloride of ammonium, oxalate and phosphate of ammonia.

4. *The Determination of the several fixed Constituents;*
5. *The Determination of the total Amount of Ammonia;*
6. *The Determination of the total Amount of Nitrogen;*
7. *The Determination of the total Amount of Carbon,*

are effected by the methods given in § 261.

8. *Determination of the Carbonic Acid.*

Genuine guano contains only a small proportion of carbonates. If therefore a guano effervesces strongly when moistened with dilute hydrochloric acid, this may be regarded as a tolerably conclusive proof of adulteration with carbonate of lime.

9. *Determination of the Uric Acid.*

If it is wished to ascertain the quantity of uric acid which a guano contains, treat the part insoluble in water with a weak solution of soda at a gentle heat, filter, and acidify the filtrate with hydrochloric acid, to precipitate the uric acid. Collect the uric acid on a weighed filter, dry, and weigh.

As the manuring value of a sample of guano may be estimated, with sufficient accuracy, by the phosphoric acid and nitrogen which it contains, the analysis may be considerably shortened, and confined to the following processes:—

a. Determination of Water (see 1).

nitrate of potassa; heat cautiously, dissolve the residue in hydrochloric acid, filter, add ammonia to the filtrate to alkaline reaction, then acetic acid until the phosphate of lime is redissolved; lastly—without previously filtering off the very trifling precipitate of sesquioxide of iron—acetate of sesquioxide of uranium, and determine the phosphoric acid as directed § 134, 1, *c.*

d. Determination of Nitrogen, by the method described § 187. As mixing the guano in the mortar with soda-lime would be attended with escape of an appreciable amount of ammonia, it is advisable to effect this operation in the combustion tube, with the aid of a wire (see § 176, fig. 104).

C. ANALYSIS OF GROUND BONES.

§ 263.

There are three sorts of bone powder.

I. The powder obtained by the grinding of fresh bones, which is generally very coarse.

II. The powder obtained by the grinding of more or less decayed bones.

III. The powder of bones which, previous to the operation of grinding, have been submitted to the action of aqueous vapors.

I. Is very coarse, and contains a relatively large proportion of fat and of gelatinous matter.

II. Is considerably poorer in organic substances.

III. Is much finer than I. and II.; it contains hardly any fat, and is still poorer in gelatinous matter than II.

1. Examine the powder, in the first place, by careful inspection, sifting, and elutriation, to ascertain the degree of comminution, and the presence of foreign matters.

2. *Determination of the Water.*—Dry a sample at 212° F.

3. *Determination of the total Amount of fixed Constituents.*—Ignite about 5 grammes, with access of air, until the ash appears white; then weigh the residue.

4. *Determination of the fixed Constituents severally.*—Treat the ash of 3 with dilute hydrochloric acid, filter off the insoluble portion (sand, &c.), and determine the sesquioxide of iron, lime, magnesia, and phosphoric acid in the solution as directed § 253.

5. *Determination of the Nitrogen.*—Ignite 0·5—0·8 grm. with soda-lime (§ 187).

6. *Determination of the Fat.*—Exhaust 5 grammes of the sample (very finely pounded), by boiling with ether, and dry the residue at 230° F. The loss of weight *minus* the mixture found in 2, shows the amount of fat. By way of control, the ether may be distilled off, and the residual fat weighed, care being taken to leave no water under the fat.

7. Deduct from the total weight the collective weight of the fixed constituents, carbonic acid, water, and fat; the difference expresses the quantity of *gelatinous matter* contained in the analysed sample.

8. Determine the *carbonic acid* as directed § 139, II., *e, a, bb.*

To increase the efficiency of basic phosphate of lime as a manuring agent, it is often treated with a certain quantity of sulphuric acid, with addition of water. This treatment causes the formation of sulphate of lime and of acid phosphate of lime, soluble in water. If 2 equivalents of hydrated sulphuric acid are used to 1 equivalent of basic phosphate of lime, the decomposition is complete; if less sulphuric acid is used, the decomposition is not complete. If the decomposed moist mass is converted into a dry powder by addition of some indifferent body, the acid phosphate of lime remains soluble in water; but if wood ashes are used for the purpose, phosphate of potassa is formed, whilst part of the soluble acid phosphate of lime is reconverted to the basic state, and becomes insoluble in water. Manures prepared in the manner described, are called *superphosphates;* they are made from calcined bones, bone ash, precipitated phosphate of lime, coprolites, and also from the powder of fresh bones. The analysis of these preparations being intended not only to show the quantities of the several constituents contained in them, but to give information also with regard to the state of solubility of these constituents, and more especially of the phosphates, the analytical process is less simple than for guano and ground bones.

1. Dry about 3 grammes of the sample at 320° F. The loss of weight expresses, *a*, the *moisture; b*, the *water of the gypsum.*

2. Boil, in a dish, 10 grammes of the sample with water, let deposit, decant the fluid on to a filter, and repeat the process of boiling, with moderate quantities of water, until the decanted fluid no longer shows acid reaction. Dilute the aqueous solution so obtained to the volume of 250 c.c., and dry the residue at about 212° F.

3. Of the *aqueous solution*, which generally appears yellow from the presence of organic matter, measure off 3 portions, α and β of 50 c.c. each; γ of 100 c.c.

α. Evaporate α in a platinum dish, adding, after some time, cautiously, thin milk of lime just to distinct alkaline reaction; proceed with the evaporation, dry the residue at 320° F., and weigh; ignite the weighed residue, and weigh again; the difference between the results of the two weighings expresses the quantity of *organic matter* in the aqueous solution. Boil the residue with pure lime-water, then with water, filter, precipitate the sulphuric acid from the filtrate by addition of a little chloride of barium, then the baryta and lime by carbonate of ammonia, and determine the *alkalies* as chlorides according to § 153, 4, *a*, β (16).

β. Precipitate β with chloride of barium, and determine the *sulphuric acid* in the usual way (§ 132, I., 1).

γ. Add to γ an excess of carbonate of soda and a little nitrate of potassa, and evaporate to dryness in a platinum dish. Ignite the residue gently, then treat with water, rinse into a beaker, add hydrochloric acid, and apply a gentle heat until complete solution is effected. Add to the clear fluid, ammonia, then acetic acid in excess; filter from the *phosphate of sesquioxide of iron*, divide the filtrate into two equal portions, and determine in one the *phosphoric acid*, by means of solution of acetate of sesquioxide of uranium (§ 134, *c*), in the other the *lime* and *magnesia* as directed § 154, 4, *b* (31).

expresses the total amount of substances insoluble in water. Moisten the residue now with a little nitric acid, ignite gently, with access of air, until the whole of the organic matter and charcoal is burnt, then weigh again; the difference between the results of the two weighings expresses the quantity of the organic matter.

5. Boil the residue of 4 with dilute hydrochloric acid; after boiling for some time, dilute with water, filter, and dilute the filtrate by means of the washing water to ½ litre; treat the insoluble residue as directed in 7.

6. Of the hydrochloric acid solution obtained in 5, measure off two portions, one of 50, the other of 100 c.c. In the former determine the *sulphuric acid*, in the latter the *phosphate of sesquioxide of iron* (if present), *lime*, *magnesia*, and *phosphoric acid*, as directed in 3, β and γ.

7. Dry, ignite, and weigh the insoluble residue of 5. It generally consists only of *sand*, *clay*, and *silicic acid*. To make quite sure, however, boil with concentrated hydrochloric acid; should some more gypsum be dissolved, determine the amount of this in the solution. Treat the insoluble residue as directed § 235, *b*, to separate the silicic acid from the clay and sand.

8. Lastly, determine the *nitrogen* in 0·8—1 grm. of the superphosphate (§ 187). As the nitrogen is already included in the weight of the organic matter, it is simply entered in the report of the results by way of information, and not as an element of the calculation.

9. Should the superphosphate contain an ammonia salt, determine the ammonia as directed § 99, 3, *a*.

VI. ANALYSIS OF ATMOSPHERIC AIR.

§ 265.

In the analysis of atmospheric air we usually confine our attention to the following constituents: oxygen, nitrogen, carbonic acid, and aqueous vapor. It is only in exceptional cases that the exceedingly minute quantities of ammonia and other gases (many of which may be assumed to be always present in very minute traces) are also determined.

It does not come within the scope of the present work to describe all the methods which have been employed in the excellent investigations made in the last few years by *Brunner*, *Bunsen*, *Dumas* and *Boussingault*, *Regnault* and *Reiset*, and others, and to which we are indebted for a more accurate knowledge of the composition of our atmosphere. Excellent descriptions of these methods will be found in *H. Rose's* "Handbuch der analytischen Chemie," vol. ii. p. 853; in *Graham's* "Chemistry;" in *Liebig*, *Poggendorff*, and *Wöhler's* "Handwörterbuch der Chemie," 2nd edit. vol. ii. p. 431; and *Bunsen's* "Gasometry," translated by *Roscoe*.

I confine myself to those methods which are found most convenient in the analysis of the air for technical or medical purposes.

A. DETERMINATION OF THE WATER AND CARBONIC ACID.

§ 266.

The determination of these two constituents of the atmosphere was formerly usually effected by *Brunner's* method, that is, by slowly drawing, constituents by the increased weight of the apparatus.

Fig. 147 represents an aspirator, constructed on *Regnault's* plan.

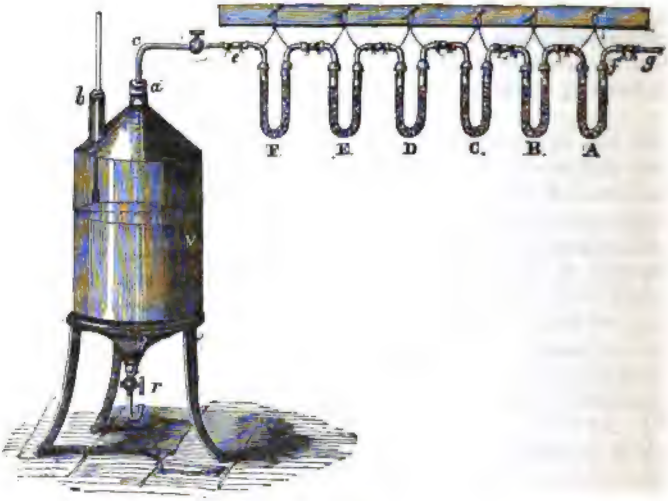

Fig. 147.

The vessel V is made of zinc-plated sheet iron, or of sheet zinc; it holds from 50 to 100 litres, and stands upon a strong tripod in a trough of sufficient capacity to contain the whole of the water. At *a* a brass tube, *c*, with stopcock is firmly fixed in with cement. Into the aperture *b*, which serves also to fill the apparatus, a thermometer reaching down to the middle of V is fixed air-tight by means of a perforated cork soaked in wax.

The efflux tube, *r*, is bent slightly upward, to guard against the least chance of air entering the vessel from below. The capacity of the vessel is ascertained by filling it completely with water, and then accurately measuring the contents in graduated vessels. The end of the tube *c* is connected air-tight with F, by means of a caoutchouc tube; the tubes A—F are similarly connected. A, B, E, and F are filled with perfectly neutral chloride of calcium; C and D with moist hydrate of potassa.* Finally, A is also connected with a long tube leading to the place from which the air intended for analysis is to be taken. The corks of the tubes are coated over with sealing wax. The tubes A and B are intended to withdraw the moisture from the air; they are weighed together. C, D, and E are also weighed jointly. C and D absorb the carbonic acid; E the aqueous vapors which the air dried in A and B may take up from the

* In the last edition I had recommended pumice stone moistened respectively with sulphuric acid and solution of potassa, instead of chloride of calcium and hydrate of potassa, as originally employed by *Brunner*. But *Hlasiwetz* ("Chem. Contralbl.," 1856, page 575) having shown that solution of potassa absorbs, besides carbonic acid, also oxygen,—a fact remarked also by *H. Rose*—and that sulphuric acid absorbs not only aqueous vapor, but also carbonic acid, I have returned to *Brunner's* original practice.

hydrate of potassa. F need not be weighed; it simply serves to protect E against the entrance of the aqueous vapors from V.

The aspirator is completely filled with water; *c* is then connected with F, and thus with the entire system of tubes of which the apparatus consists; the cock *r* is opened a little, just sufficient to cause a slow efflux of water. As the height of the column of water in V is continually diminishing, the cock must from time to time be opened a little wider, to maintain as nearly as possible a uniform flow of water. When V is completely emptied, the height of the thermometer and that of the barometer are noted, and the tubes A and B, and C, D, and E weighed again.

As the increase of weight of A and B gives the amount of water, that of C, D, and E, the amount of carbonic acid in the air which has passed through them; and as the volume of the latter (freed from water and carbonic acid) is accurately known from the ascertained capacity of V:* the calculation is in itself very simple; but it requires, at least in very accurate analyses, the following corrections:—

a. Reduction of the air in V, which is saturated with aqueous vapor, to dry air; since the air which penetrates through *c* is dry (see § 198, γ).

β. Reduction of the volume of dry air so found, to 32° F., and 760 millimetres bar. (§ 198, a and β).

When these calculations have been made, the weight of the air which has penetrated into V is readily found (1000 c.c. of dry air at 32° F., and 760 millimetres bar., weighing 1·29366 grm.); and as the carbonic acid and water have also been weighed, the respective quantities of these constituents of the air may now be expressed in per cents. by weight or, calculating the weight in volumes, in per cents. by measure or volume.

Considering the great weight and size of the absorption apparatus, in comparison to the increase of weight by the process, at least 25,000 c.c. of air must be passed through; the air inside the balance-case must be kept perfectly dry by means of a sufficient quantity of chloride of calcium, and the apparatus left for some time in the balance-case, before proceeding to weigh. Neglect of these precautions would lead to considerable errors, more particularly as regards the carbonic acid, the quantity of which in atmospheric air is, on an average, about 10 times less than that of the aqueous vapor (compare *Hlasiwetz*, "Chem. Centralbl.," 1856, page 575).

The determination of the *carbonic acid* in atmospheric air may be effected with much greater accuracy by the following method, recommended by *Fr. Mohr*, and most carefully tested by *H. von Gilm* ("Chem. Centralbl.," 1857, page 760). The aspirator employed in this method, holding at least 30 litres, is arranged like that shown in fig. 147, but has, besides *a* and *b*, a third aperture, which bears a small manometer. The air is made to pass through a tube, 1 metre long, and about 15 millimetres wide; this tube is drawn out thin at the upper end, and at the lower end bent at an angle of 140—150 degrees. It is more than half filled with coarse fragments of glass and perfectly clear baryta water, and fixed in such a position that the long part of it inclines to the horizontal line at an angle of 8—10 degrees. A narrow glass tube fitted into the lower end of the tube by means of a perforated cork, serves to retained. When about 60 litres of air have slowly passed through the absorption tube, the carbonate of baryta formed is filtered off out of contact of air, and the tube as well as the contents of the filter washed, first with distilled water saturated with carbonate of baryta, then with pure boiled water. The carbonate of baryta in the filter and in the tube is then dissolved in dilute hydrochloric acid, the solution evaporated to dryness, the residue gently ignited, the chlorine of the chloride of barium determined as directed § 141, *b*, *a*, and 1 equivalent of carbonic acid entered for 1 equivalent of chlorine. As will be readily seen, the baryta in the hydrochloric acid solution may also be determined by precipitating with sulphuric acid. For filtering the carbonate of baryta, *Gilm* employs a double funnel (see Fig. 148). The inner cork has, besides the perforation through which the neck of the funnel passes, a lateral slit, which serves to establish a communication between the air in the outer funnel and the air in the bottle.

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* Or from the quantity of water which has flown from V, as the experiment may be altered in this way, that a portion only of the water is allowed to run off, and received into a measuring vessel.

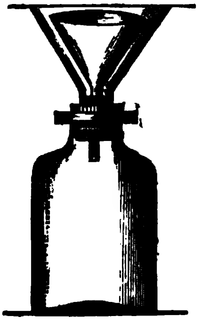
Fig. 148.

As, with the absorption apparatus arranged as described, the air has to force its way through a column of fluid, the manometer in the third aperture of the aspirator is required to determine the actual volume of the air; the height indicated by this instrument being deducted from the barometric pressure observed during the process.

Pettenkofer (*Liebig*, *Poggendorff*, and *Wöhler's* "Handwörterbuch der Chemie," 2nd edition, vol. ii., page 445) has recently recommended the following simple and expeditious method of determining with sufficient accuracy the carbonic acid in atmospheric air.

Take a perfectly dry bottle, of about 6 litres capacity, with well-fitting ground glass stopper, and accurately determine the capacity; fill the bottle, by means of a pair of bellows, with the air to be analysed; add 45 c.c. of clear lime-water of known strength, determined by means of standard oxalic acid, and cause the lime-water to spread over the inner surface of the bottle, by turning the latter about, but without much shaking. In the course of about ½ an hour the whole of the carbonic acid is absorbed. Pour the turbid lime-water into a cylinder, close securely, and let deposit; then take out, by means of a pipette, 30 c.c. of the clear supernatant fluid, determine the lime in this by standard oxalic acid, multiply the volume used by 1·5 (as only 30 c.c. of the original 45 are employed in this experiment), and deduct the result from the amount of lime originally present in the 45 c.c. of lime-water; the difference expresses the quantity of lime converted into carbonate; calculate the carbonic acid from this. If the air is unusually rich in carbonic acid, the quantity of lime-water used is correspondingly increased. *Pettenkofer* uses a standard oxalic acid containing, at 63·5° F., 2·250 grammes of crystallized oxalic acid in the litre; 1 c.c. of this solution saturates 0·001 grm. of lime. The point of neutralization is recognised most accurately, by letting a drop of the fluid fall upon turmeric paper, and observing whether a brown coloration appears round the drop.

B. Determination of the Oxygen and Nitrogen.

§ 267.

Among the many methods recommended for determining the oxygen of the air, I select the one which I deem best suited for the purpose—viz., *Liebig's* ("Annal. d. Chem. u. Pharm.," 77, 107).

This method is based upon the observation made by *Chevreul* and *Döbereiner*, that pyrogallic acid, in alkaline solutions, has a powerful tendency to absorb oxygen.

1. A strong measuring tube, holding 30 c.c. and divided into $\frac{1}{5}$ or $\frac{1}{10}$ c.c., is filled to $\frac{2}{3}$ with the air intended for analysis. The remaining part of the tube is filled with mercury, and confined over that agent in a tall cylinder, widened at the top (Fig. 114, § 184).

2. The volume of air confined is measured (§ 12). If it is intended to determine the carbonic acid—which can be done with sufficient accuracy only if the quantity of the acid amounts to several per cents.—the air is dried by means of a ball of chloride of calcium introduced into it (§ 16), and then again measured. If it is not intended to determine the carbonic acid, this operation is omitted. A quantity of solution of potassa of 1·4 specific gravity (1 part of dry hydrate of potassa to 2 parts of water), amounting to from $\frac{1}{40}$ to $\frac{1}{50}$ of the volume of the air, is then introduced into the measuring tube by means of a pipette with the point bent upward (see Fig. 149), and spread over the entire inner surface of the tube by shaking the latter (§ 184 *a a*); when no further diminution of volume takes place, the decrease is read off. If the air has been dried previously with chloride of calcium, the diminution of the volume expresses exactly the amount of carbonic acid contained in the air; but if it has not been dried with chloride of calcium, the diminution in the volume cannot afford correct information as to the amount of the carbonic acid, since the strong solution of potassa absorbs also aqueous vapor.

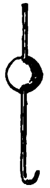

Fig. 149.

3. When the carbonic acid has been determined (or simply removed), a solution of pyrogallic acid, containing 1 gramme of the acid in 5 or 6 c.c. of water,* is introduced into the same measuring tube by means of another pipette, similar to the one used in 2 (Fig. 149); the quantity of pyrogallic acid employed should be half the volume of the solution of potassa used in 2. The mixed fluid (the pyrogallic acid and solution of potassa) is spread over the inner surface of the tube by shaking the latter, and, when no further diminution of volume is observed, the residuary nitrogen is measured.

4. The solution of pyrogallic acid mixing with the solution of potassa, of course dilutes it, causing thus an error from the diminution of its tension; but this error is so trifling that it has no appreciable influence upon the results; it may, besides, be readily corrected, by introducing into the tube, after the absorption of the oxygen gas, a small piece of hydrate of potassa corresponding to the amount of water in the solution of the pyrogallic acid.

5. There is another source of error in this method; viz., on account of

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* *Liebig* has recently described a very advantageous method of preparing pyrogallic acid. See "Annal. d. Chem. u. Pharm.," 101, 47.

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comparative analyses, the influence of this defect upon the results may be almost entirely neutralized, by taking nearly equal volumes of air in the several analyses.*

6. Notwithstanding these sources of error, the results obtained by this method are very accurate and constant. In eleven analyses which *Liebig* reports, the greatest difference in the amount of oxygen found was between 20·75 and 21·03. The numbers given express the actual and uncorrected results.

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* As stated, § 210, *Bunsen* employs for the absorption of oxygen gas, a *Papier mâché* ball saturated with a concentrated alkaline solution af pyrogallate of potassa, which he introduces into the gaseous mixture attached to a platinum wire. By adopting this proceeding, the source of error mentioned in 5 is avoided.

PART III.

EXERCISES FOR PRACTICE.

EXERCISES FOR PRACTICE.

I HAVE given here 52 exercises for practice. The exercises selected are nearly the same as I have for some sessions past been in the habit of giving to the students in my laboratory; I can therefore safely affirm that all of them may be readily performed, and also that the order of succession in which they are arranged has been found practically useful. As regards the order of succession in which the exercises are arranged, I have departed from the rule laid down in this respect in the last edition. Instead of directing the student to go through the entire series of gravimetrical analyses, before attempting a volumetrical analysis, I have, in the present edition, after the first 13 numbers, adopted to a certain extent, the system of alternation, interspersing the gravimetrical occasionally with volumetrical analyses.

The principal point I had in view in the selection of these exercises, was that most of them, and more particularly the gravimetrical analyses, should permit an exact control of the results. This is of the utmost importance for the student, since a certain degree of confidence in the correctness of the results of one's own experiments is among the most indispensable requisites for a successful pursuit of quantitative investigations; and a confidence of this kind can, in my opinion, only be attained by affording the student the means of testing and controlling the accuracy of the results obtained in his experiments.

Now, a rigorously accurate control is practicable only in the analysis of pure salts of known composition, or of substances which the analyst himself has previously prepared, and of which he knows the constituents and the relative proportions in which they are combined. When the student has acquired, in the analysis of such substances, the necessary degree of confidence in his own abilities, he may gradually proceed to analyses of minerals and products of industry; and to other processes of a more difficult and intricate nature, in which a very rigorous control is not practicable.

The second point which I had in view in the selection of these exercises for practice, was to make them comprise both the more important analytical methods and the most important compounds, so as to afford the student proper opportunities to acquire a thorough knowledge of every branch of quantitative analysis. I have therefore not always indicated the most simple methods.

Organic analysis offers far less variety than the analysis of inorganic substances—the exercises relating to the former branch are therefore less numerous here than those relating to the latter. I would advise the student to analyse the same organic substance repeatedly until the results prove quite satisfactory.

In conclusion, I have to remark that I do not mean to insist upon the without having ever tried *every* method or analysed *every* compound. I would, however, warn students to guard against prematurely attempting new discoveries. The safest way is to wait until he has acquired a certain degree of proficiency in general chemistry, and more particularly in practical analysis.

EXERCISES.

A. SIMPLE DETERMINATIONS IN THE GRAVIMETRICAL WAY, INTENDED TO PERFECT THE STUDENT IN THE PRACTICE OF THE MORE COMMON ANALYTICAL OPERATIONS.

1. IRON.

Weigh, on a watch-glass, about 0·3 grm. of fine pianoforte wire, and dissolve in hydrochloric acid, with addition of nitric acid. The acids are diluted with a little water.

The solution is effected by boiling in a moderate sized flask covered with a watch-glass. When complete solution has ensued, and the color of the fluid shows that all the iron is dissolved as sesquioxide (if this is not the case some more nitric acid must be added), rinse the watch-glass, dilute the fluid in the flask, heat to incipient ebullition, add ammonia in moderate excess, filter, &c. (Compare § 113, 1 *a*).

After weighing the sesquioxide of iron, dissolve by digesting with fuming hydrochloric acid, to ascertain whether it contains silicic acid; if silicic acid is found, determine this, and deduct the result from the weight of the sesquioxide of iron.

The following example will show the best way of reporting the results :—

Watch-glasses + iron	10·3192
„ empty	9·9750
Iron	0·3442
Crucible + sesquioxide of iron	17·0673
„ empty	16·5761
	0·4912
Filter-ash No. 2	0·0012
Sesquioxide of iron	0·4900 =
Iron	0·343 = 99·65 pr cnt.

2. ACETATE OF LEAD.

Determination of Oxide of Lead.—Triturate the dry and non-effloresced crystals in a porcelain mortar, and press the powder between sheets of blotting paper until the last sheets are no longer moistened by it.

a. Weigh about 1 gramme, dissolve in water, with addition of a few drops of acetic acid, and proceed exactly as directed § 116, 1, *a*, *a*.

b. Weigh about 1 gramme, and proceed exactly as directed § 116, *5* (*Dulk's* modification of *Berzelius's* method).

Pb O	1394·64	111·57	58·85
$\bar{A}$	637·50	51·00	26·91
3 aq	337·50	27·00	14·24
	2369·64	189·57	100·00

3. ARSENIOUS ACID.

Dissolve about 0·4 grm. of pure arsenious acid in small lumps in a middle-sized flask, with a glass stopper, in some solution of soda, by digesting the mixture on the water-bath; dilute with a little water, add hydrochloric acid in excess, and then nearly fill the flask with sulphuretted hydrogen water. Insert the stopper and shake. If the sulphuretted hydrogen is present in excess, the precipitation is terminated; if not, conduct an excess of sulphuretted hydrogen gas into the fluid; proceed in all other respects exactly as directed § 127, 4.

As	937·5	75	75·76
O_3	300·0	24	24·24
	1237·5	99	100·00

4. POTASSA ALUM.

Determination of the Alumina.—Press pure triturated potassa alum between sheets of blotting paper; weigh off about 2 grammes, dissolve in water, and determine the alumina as directed § 105, *a.*

KO	588·86	47·11	9·93
Al_2O_3	640·84	51·26	10·81
4 SO_3	2000·00	160·00	33·73
24 HO	2700·00	216·00	45·53
	5929·70	474·37	100·00

5. CRYSTALLIZED SULPHATE OF MAGNESIA.

a. Determination of the Magnesia.—Triturate and dry as directed § 26, *a.* Dissolve from 1 to 2 grammes in water, and determine the magnesia as directed § 104, 2.

Mg O	250·19	20	16·26
SO_3	500·00	40	32·52
7 aq	787·50	63	51·22
	1537·69	123	100·00

6. CHLORIDE OF SODIUM.

Determination of the Chlorine.—Fuse pure chloride of sodium in a platinum crucible, pour the fused mass upon a piece of porcelain, break whilst still hot into pieces, and preserve these in a well-corked glass tube. Dissolve about 0.4 grm. in water, and determine the chlorine as directed § 141, I., *a.*

For the per-centage composition, see § 69.

7. Carbonate of Lime.

Heat pure carbonate of lime in powder (no matter whether calcareous spar or artificially prepared carbonate of lime) gently in a platinum crucible.

a. Determination of the Lime.—Dissolve, in a covered beaker, about 1 gramme in dilute hydrochloric acid, heat gently until the carbonic acid is completely expelled, and determine the lime as directed § 103, 2, *b.*

b. Determination of the Carbonic Acid.—Determine in about 0·8 grm. the carbonic acid according to the directions of § 139, II., *d.*

For the composition, see § 73.

8. Sulphate of Copper.

(Complete Analysis of Sulphate of Copper.)

Triturate the pure crystals in a porcelain mortar, and press the powder between sheets of blotting paper.

a. Determination of the Water of Crystallization.—Weigh an empty bulb tube, and half fill the bulb with sulphate of copper ;[*] weigh again, then place the tube in an air-bath with openings in its sides (Fig. 33), and proceed as directed § 29. When no more water escapes at 248° to 284° F., and repeated weighings of the bulb tube give constant results, the diminution of weight expresses the amount of crystallization water in the salt. A common glass tube of sufficient width may be used instead of a bulb tube, the sulphate of copper being placed in a little boat, and the latter inserted into the tube. To guard against the reabsorption of water during the process of weighing, the little boat should be placed in a small tube, closed by a cork, and this tube weighed with it both before and after weighing.

b. Determination of the Water of Halhydration.—Proceed with the same experiment, but at a temperature raised to between 482° F. and 500° F. The additional loss of weight of the bulb tube suffered in this process, gives the amount of the more strongly combined halhydration water.

c. Determination of the Sulphuric Acid.—In another portion of the sulphate of copper (about 1·5 grm.) determine the sulphuric acid according to the directions of § 132, I., 1.

d. Determination of the Oxide of Copper.—In about 1·5 grm. determine the oxide of copper as directed § 119, 1, *a*, *a*.

CuO	496·0	39·68	31·83
SO_3	500·0	40·00	32·08
HO	112·5	9·00	7·22
4 aq	450·0	36·00	28·87
	1558·5	124·68	100·00

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[*] This is effected by pushing into one end of the tube, down to the bulb, a glass rod with paper folded round it, and filling in the salt through the other end. The tube is then restored to a horizontal position, and the bulb gently tapped on the table ; the glass rod is withdrawn, and the ends are, if necessary, cleaned with a feather.

9. CRYSTALLIZED PHOSPHATE OF SODA.

a. Determination of the Water of Crystallization.—Heat about 1 grm. in a platinum crucible, slowly and gently (not to ignition); the loss of weight gives the amount of water of crystallization in the compound.

b. Determination of the Basic Water.—Ignite the residue of *a.*

c. Determination of the Soda and the Phosphoric Acid.—Treat the residue of *b* as directed § 135, *a*, *γ*.

d. Determination of the Phosphoric Acid by way of Control.—Treat 1·5—2 grms. of the salt as directed § 134, I., *b*, *a*.

PO_5	887·50	71·00	19.83
$2NaO$	774·88	62·00	17·32
HO	112·50	9·00	2·51
24 aq	2700·00	216·00	60·34
	4474·88	358·00	100·00

6253
62.17
.08
[illegible] .7435

10. PHOSPHATE OF AMMONIA AND MAGNESIA.

Dry in the exsiccator (see § 27, at the end).

a. Water and Ammonia.—Ignite about 1 grm. of the salt, and determine the loss of weight.

b. Ammonia.—Treat about 1 grm. of the salt as directed § 99, 2 (method *β*).

c. Phosphoric Acid.—Treat about 1 grm. of the salt as directed in § 134, *c*, and about 0·5 grm. as directed § 134, *b*, *β*.

d. Magnesia.—Treat about 1 grm. of the salt as directed § 135, *d*.

PO_5	887·50	71·00	28·98
$2MgO$	500·38	40·00	16·33
NH_4O	325·06	26·00	10·61
12 aq	1350·00	108·00	44·08
	3062·94	245·00	100·00

11. CINNABAR.

Reduce to a fine powder by trituration, and dry at 212° F.

a. Determination of the Sulphur.—Pour strong hydrochloric acid over about 0·5 grm. of the sulphide, in a little flask, add from time to time small portions of chlorate of potassa, expose for some time to the action of a very gentle heat, with proper escape for the vapors, and proceed as directed § 148, II., *a*, *β*.

b. Determination of the Mercury.—Dissolve about 0·5 grm. as before, dilute, and let the mixture stand in a moderately warm place until the smell of chlorine has nearly gone off; filter if necessary, add ammonia in excess, heat gently for some time, add hydrochloric acid until the white precipitate of chloride of mercury and amide of mercury is redissolved, and treat the solution, which now no longer smells of chlorine, as directed § 118, 3.

For the per-centage composition, see § 84, *c*.

12. CRYSTALLIZED GYPSUM.

Select pure native crystallized gypsum, triturate, and dry under the exsiccator (§ 27).

CaO	350	28	32·56
SO_3	500	40	46·51
2 aq.	225	18	20·93
	1075	86	100·00

C. SEPARATION OF TWO BASES OR TWO ACIDS FROM EACH OTHER, AND DETERMINATIONS IN THE VOLUMETRICAL WAY.

13. SEPARATION OF IRON FROM MANGANESE.

Dissolve in hydrochloric acid about 0·5 grm. of fine pianoforte wire, and about the same quantity of ignited protosesquioxide of manganese (prepared as directed § 109, 1); heat with a little nitric acid, and separate the two metals by means of acetate of soda (§ 160, 80). Determine the manganese as directed § 109, 1, *a.*

14. VOLUMETRIC DETERMINATION OF IRON BY SOLUTION OF PERMANGANATE OF POTASSA.

a. Determination of the Strength of the Solution of Permanganate of Potassa.

α. By metallic iron, § 112, 2, *a, aa.*
β. By sulphate of protoxide of iron and ammonia, § 112, 2, *a, α, bb.*
γ. By oxalic acid, § 112, 2, *a, α, cc.*

b. Determination of Iron in Brown Hematite (§ 240).

15. DETERMINATION OF NITRIC ACID IN NITRATE OF POTASSA.

Dry at 212° F.—Proceed as directed § 149, II., *a, α.*
For the per-centage composition, see § 68, *b.*

16. SEPARATION OF MAGNESIA FROM SODA.

Dissolve in dilute hydrochloric acid about 0·4 grm. of pure recently ignited magnesia* and about 0·5 grm. of pure fused chloride of sodium, and separate the alkali from the earth, by means of oxalic acid, as directed § 153 (18).

17. SEPARATION OF POTASSA FROM SODA.

Press between blotting paper, triturated crystallized tartrate of potassa and soda (Rochelle salt), weigh off about 1·5 grm., heat in a platinum crucible, gently at first, then to ignition, and complete combustion of the separated charcoal. Dissolve the residue in water, determine the alkalies jointly as chlorides (§ 97, 3), then separate them by bichloride of platinum (§ 152, 1), and calculate from the results the quantities of soda and potassa severally contained in the Rochelle salt.

KO	588·86	47·11	16·70
NaO	387·44	31·00	10·99
$C_8H_4O_{10}$	1650·00	132·00	46·79
8 aq	900·00	72·00	25·52
	3526·30	282·11	100·00

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* This may be prepared most readily by exposing pure oxalate of magnesia to the action of heat (*F. Schulze*).

18. VOLUMETRICAL DETERMINATION OF CHLORINE IN CHLORIDES.

a. Preparation and examination of the solution of chloride of sodium and nitrate of silver (§ 141, I., *b*, *a*).

b. Indirect determination of the soda and potassa in Rochelle salt, by volumetrical estimation of the chlorine in the alkaline chlorides prepared as in No. 17. Calculation, see § 200, *a*, *β*.

19. SEPARATION OF ZINC FROM CADMIUM.

Dissolve in hydrochloric acid about 0·4 grm. of pure oxide of cadmium, and about the same quantity of pure oxide of zinc, both recently ignited, and separate the metals as directed § 162 (**107**).

20. ACIDIMETRY.

a. Preparation of standard oxalic acid, standard sulphuric acid, and standard solution of soda (§ 215).

b. Determination of free acid in hydrochloric acid, by the specific gravity (§ 209 and § 214, Table II.),

c. Determination of free acid in the same hydrochloric acid, by saturation with an alkaline fluid of known strength (§ 215).

d. Determination of free acid in colored vinegar, by saturation with an alkaline standard solution (application of test papers).

e. Preparation of an ammoniacal solution of sulphate of copper (§ 216); determination of its strength by standard sulphuric acid; estimation of the free acid in the hydrochloric acid used in *b* and *c*, by means of the ammoniacal solution of sulphate of copper; in this latter process the student may also add to the hydrochloric acid, some neutral sulphate of zinc.

21. ALKALIMETRY.

a. Preparation of the test acid by *Descroizelles* and *Gay-Lussac's* process (§ 219).

b. Estimation of potassa in potash of commerce after expulsion of the water by gentle ignition.

α. By *Descroizelles* and *Gay-Lussac's* method (§ 219).

β. By *Mohr's* method (§ 220).

22. DETERMINATION OF AMMONIA.

Treat about 0·8 grm. of chloride of ammonium as directed § 99, 3, *a*. For the per-centage composition, see § 70.

23. SEPARATION OF MERCURY FROM LEAD.

Dissolve about 0·5 grm. of chloride of mercury and about 1 grm. of crystallized acetate of lead, and separate the metals as directed § 163 (**132, 133**).

24. SEPARATION OF IODINE FROM CHLORINE

a. Dissolve about 0·2 grm. of iodide of potassium and about 0·6 grm. of chloride of sodium, and determine the iodine and chlorine in the mixture as directed § 169 (**222**). Calculation, see § 200, *c*.

b. Determine in a similar mixture the iodine and chlorine as directed § 169 (**225**).

25. ANALYSIS OF BRASS.

Brass is a compound of from 25 to 35 per cent. of zinc and from 65 to 75 per cent. of copper. Besides these two essential constituents, it contains usually also small quantities of tin and lead.

a. Dissolve about 2 grammes in nitric acid. Do not use more of the acid than is absolutely necessary, as the excess must be driven off by evaporation.

If an insoluble residue remains (binoxide of tin), filter the fluid—after previous dilution with water—from this residue (§ 164, **148**). Add to the filtrate, or, if the quantity of the tin is only very inconsiderable, directly to the solution, about 20 c.c. of dilute sulphuric acid; evaporate the mixture to dryness on the water-bath, add 50 c.c. of water, and apply heat. If a residue remains (sulphate of lead), filter, and proceed as directed § 116, 2. In the filtrate, separate the copper from the zinc by hyposulphite of soda as directed § 162 (**112**).

b. In about 1 grm. of the alloy determine, after removal of the tin and lead as in *a*, the copper as directed § 119, 2.

26. ANALYSIS OF SOLDER (TIN AND LEAD).

Introduce about 1·5 grm. of the alloy, cut into small pieces, into a flask, pour nitric acid over it, and proceed as directed § 164 (**148**), to effect the separation and estimation of the tin.

Mix the filtrate in a porcelain dish with pure dilute sulphuric acid, evaporate the nitric acid on the water-bath, and proceed with the sulphate of lead obtained as directed § 116, 2. Test the fluid filtered from the sulphate of lead with sulphuretted hydrogen and sulphide of ammonium for the other metals which the alloy might contain besides tin and lead.

27. ANALYSIS OF ALLOYS OF SILVER AND COPPER.

Determine the silver by the volumetrical method (§ 115, 5).

28. ANALYSIS OF A DOLOMITE.

See § 237.

29. VOLUMETRICAL DETERMINATION OF LIME IN CALCAREOUS SPAR.

See § 223.

30. ANALYSIS OF FELSPAR.

a. Decomposition by carbonate of soda (§ 140, II., *b*); removal of the silicic acid; separation of the alumina from the small quantity of sesquioxide of iron usually present, by one of the methods recommended for the purpose in § 160.

b. Decomposition by hydrofluoric acid gas (§ 140, II., *b*, β); determination of the potassa. After evaporating with sulphuric acid and dissolving the residue in hydrochloric acid and water, add, cautiously, as chloride of barium as long as a precipitate forms, then—without filtering—carbonate of ammonia and ammonia. Let the precipitate subside in the cold, then filter, evaporate the filtrate to dryness, ignite the tion, and determine the potassa finally as directed §

31. ANALYSIS OF GALENA.

a. Determination of the sulphur, lead, iron, &c.,
b. Determination of silver in galena by cupellatio

32. ANALYSIS OF MIXED SILICAT

See § 235. The special plan of proceeding is lef the student.

33. ANALYSIS OF CLAYS.

See § 236.

34. ANALYSIS OF MINERAL WAT

See §§ 206—213. The determination of constitu very minute quantities may be omitted.

35. ANALYSIS OF ASHES OF PLAN

See §§ 249—256.

36. ANALYSIS OF SOILS.

See §§ 257—259.

37. DETERMINATION OF CHLORINE IN CHLORIDE

a. By *Penot's* method (§ 227).
b. By *Bunsen's* method.
α. Preparation of the iodine solution, § 146.
β. Determination of the strength of the iodine solı
aa. By pure iodine (§ 146, 1, *c*, *β*, *aa*).
bb. By chromate of potassa (§ 146, 1, *c*, *β*, *bb*).
γ. Examination of chloride of lime (see D, § 228).

38. DETERMINATION OF BINOXIDE IN MANGANES

a. By *Fresenius* and *Will's* method (§ 230, A).
b. By *Bunsen's* method (§ 230, B).
c. By means of iron (§ 230 C).

39. ANALYSIS OF GUNPOWDER.

See § 234.

40. DETERMINATION OF SUGAR IN FRUIT, HON

See § 247, sqq.

E. DETERMINATION OF THE SOLUBILITY OF

41. DETERMINATION OF THE DEGREE OF SOL COMMON SALT.

a. At boiling heat 229·46° F.—Dissolve perfectl chloride of sodium in distilled water, in a glass flask ; to boiling, and keep in ebullition until part of separates. Filter the fluid now with the greatest accurately tared capacious measuring flask, through a with boiling water and covered with a glass plate.

of the fluid, by evaporating in a platinum dish (best with addition of some chloride of ammonium, which will, in some measure, prevent decrepitation); or by determining the chlorine (§ 141).

b. At 57·2°.—Allow the boiling saturated solution to cool down to 57·2° F. with frequent shaking, and then proceed as in *a.*

100 parts of water dissolve at 229·46° F. . 40·35° of chloride of sodium.
100 „ „ 57·2° . 35·87° „ „

42. Determination of the Degree of Solubility of Sulphate of Lime.

a. In water of 212° F.
b. In water of 53·6° F.

Digest pure pulverized sulphate of lime for some time with water, in the last stage of the process at a temperature of 104°—122° F. (at which temperature sulphate of lime is most soluble); shake the mixture frequently during the process. Decant the clear solution, together with a little of the precipitate, into two flasks, and boil the fluid in one of them for some time; allow that in the other to cool down to 53·6° F., with frequent shaking, and let it stand for some time at that temperature. Then filter both solutions, weigh the filtrates, and determine the amount of sulphate of lime respectively contained in them, by evaporating the fluids and igniting the residues.

100 parts of water dissolve at 212° F. . . . 0·217 of anhydrous sulphate of lime.
100 „ „ 53·6° F. . . . 0·233 „ „

F. Determination of the Solubility of Gases in Fluids, and Analysis of Gaseous Mixtures.

43. Determination of the Absorption-Coefficient of Sulphurous Acid.

See "Annal. d. Chem. u. Pharm.," vol. 95, page 1; also § 131, 2.

44. Analysis of Atmospheric Air.

See §§ 265—267.

G. Organic Analysis and Determinations of the Equivalents of Organic Bodies.

45. Analysis of Cane Sugar.

Select perfectly pure white crystals. Triturate, and dry at 212° F.
a. Burn with oxide of copper, by *Liebig's* method (§§ 174, 175).
b. Burn with oxide of copper, by *Bunsen's* method (§ 176).

12 C	900·00	72	42·10
11 H	137·50	11	6·44
11 O	1100·00	88	51·46
	2137·50	171	100·00

OF POTASSIUM.

Triturate the perfectly pure crystals, dry the pow (§ 27), and determine the nitrogen as directed § 1 formula demands 19·87 per cent. of nitrogen.)

47. ANALYSIS OF URIC ACID (or any other pe compound of carbon, hydrogen, oxygen, and nitroge

Dry pure uric acid at 212° F.

a. Determination of the carbon and hydrogen (§

b. Determination of the nitrogen.

α. See § 186 and § 187.

β. By *Dumas's* method (§ 185).

5 C	375	30
2 N	350	28
2 H	25	2
3 O	300	24
	1050	84

48. ANALYSIS OF COAL.

a. Determination of the water by drying at 230°

b. Determination of the carbon, hydrogen, and a sample, in a porcelain boat, in a current of oxy small proportion of sulphur and nitrogen contain no particular precautions in the process.

c. Determination of the nitrogen (§ 186 and § 18

d. Determination of the sulphur, by one of the § 188.

49. ANALYSIS OF OIL OF TURPENT

Select for the analytical process oil of turpenti perfectly freed from water by digestion with fused and recently rectified. Method, § 181.

5 C	375	30
4 H	50	4
	425	34

50. ANALYSIS AND DETERMINATION OF THE E BENZOIC ACID.

Complete analysis of benzoate of silver. *a.* D silver as directed § 115, 1 or 4; *b.* Determination hydrogen, by any suitable method. Calculation, § 2

51. ANALYSIS AND DETERMINATION OF THE EQ ORGANIC BASE.

Analysis of the base and its double salt with pla § 203, 3.

52. DETERMINATION OF THE DENSITY OF CAM

Method described § 193. Calculation, § 204.

APPENDIX.

I. ANALYTICAL NOTES AND EXP

1. Action of Water upon Glass and Porcel
Process of Evaporation (to § 41).

A large bottle was filled with water cautiously di
steam apparatus with a tin condensing tube. All
were made with this water.

a. 300 c.c., cautiously evaporated in a platinum
weighing, after ignition, 0·0005 grm. = 0·0017 per

b. 600 c.c. were evaporated, boiling, nearly to dr
of Bohemian glass; the residue was transferred to
the flask rinsed with 100 c.c. of distilled water, whi
residue in the dish, the fluid in the latter was then e
and the residue ignited.

After ignition, the residue weighed . .
Deducting from this the quantity of fixed ma
originally contained in the distilled water, viz

There remains substance dissolved out of the glas
= 0·0153 per 1000.

In three other experiments, made in the same ma
two 0·0049 grm., in the third 0·0037 grm.; which
c.c., gives an average of . . .
And after a deduction of . . .

= 0·013 per 1000.

We may therefore assume that 1 litre of water
tracted boiling in glass vessels, about 14 milligramme
of the glass.

c. 600 c.c. were evaporated nearly to dryness in a
lain, and in all other respects treated as in *b.*

The residue weighed . . .
Deducting from this the quantity of fixed matter c
tained in the distilled water, viz. . .

There remains substance dissolved out of the porcel
= 0·0005 per 1000.

2. ACTION OF HYDROCHLORIC ACID UPON GLASS AND PORCELAIN VESSELS, IN THE PROCESS OF EVAPORATION (to § 41).

The distilled water used in 1 was mixed with $\frac{1}{10}$ of pure hydrochloric acid.

a. 300 grms., evaporated in a platinum dish, left 0·002 grm. residue.

b. 300 grammes, evaporated first in Bohemian glass nearly to dryness, then in a platinum dish, left 0·0019 residue; the dilute hydrochloric acid, therefore, had not affected the glass.

c. 300 grammes, evaporated in Berlin porcelain, &c., left 0·0036 grm., accordingly, after deducting 0·002, 0·0016 = 0·0053 per 1000.

d. In a second experiment made in the same manner as in *c.*, the residue amounted to 0·0034, accordingly, after deducting 0·002, 0·0014 = 0·0047 per 1000.

Hydrochloric acid, therefore, affects glass much less than water, whilst porcelain is about equally affected by water and dilute hydrochloric acid. This shows that the action of water upon glass causes the formation of soluble basic silicates.

3. ACTION OF SOLUTION OF CHLORIDE OF AMMONIUM UPON GLASS AND PORCELAIN VESSELS, IN THE PROCESS OF EVAPORATION (to § 41).

In the distilled water of 1, $\frac{1}{10}$ of chloride of ammonium was dissolved, and the solution filtered.

a. 300 c.c., evaporated in a platinum dish, left 0·006 grm. of fixed residue.

b. 300 c.c., evaporated first nearly to dryness in Bohemian glass, then to dryness in a platinum dish, left 0·0179 grm.; deducting from this 0·006 grm., there remains substance dissolved out of the glass, 0·0119 = 0·0397 per 1000.

c. 300 c.c., treated in the same manner in Berlin porcelain, left 0·0178; deducting from this 0·006, there remains 0·0118 = 0·0393 per 1000.

Solution of chloride of ammonium, therefore, strongly affects both glass and porcelain in the process of evaporation.

4. ACTION OF SOLUTION OF CARBONATE OF SODA UPON GLASS AND PORCELAIN VESSELS (to § 41).

In the distilled water of 1, $\frac{1}{10}$ of pure crystallized carbonate of soda was dissolved.

a. 300 c.c., supersaturated with hydrochloric acid and evaporated to dryness in a platinum dish, &c., left 0·0026 grm. of silicic acid = 0·0087 per 1000.

b. 300 c.c. were gently boiled for three hours in a glass vessel, the evaporating water being replaced from time to time; the tolerably concentrated liquid was then treated as in *a*; it left a residue weighing 0·1376 grm.; deducting from this the 0·0026 grm. left in *a*, there remains 0·135 grm. = 0·450 per 1000.

c. 300 c.c., treated in the same manner as in *b*, in a porcelain vessel, left 0·0099; deducting from this 0·0026 grm., there remains 0·0073 = 0·0243 per 1000.

Which shows that boiling solution of carbonate of soda affects glass very strongly, and porcelain also in a very marked manner.

5. WATER DISTILLED FROM GLASS VESSELS (to § 56, 1).

42·41 grammes of water distilled with extreme caution from a tall

6. Sulphate of Potassa and Alcohol (to § 6

a. Ignited pure sulphate of potassa was diges alcohol, for several days, with frequent shaking of was filtered off, the filtrate diluted with water, chloride of barium. It remained perfectly clear this re-agent, but after the lapse of a considerable t a slight opalescence. Upon evaporation to dry very trifling residue, which gave, however, disti presence of sulphuric acid.

b. The same salt treated in the same manner, wit concentrated sulphuric acid, gave a filtrate which, platinum dish, left a clearly perceptible fixed residu

7. Deportment of Chloride of Potassium i High Temperature (to § 68, *c.*)

0·9727 grm. of ignited (not fused) pure chloride for 10 minutes to dull redness in an open platinum the salt was then kept for 10 minutes longer at t when no further diminution of weight was observ redness and semi-fusion, the salt suffered a further extent of 0·0009 grm. Ignited intensely and to 0·0034 grm., in addition to the former 0·0007 and

Eighteen hours' exposure to the air produced no of weight.

8. Solubility of Potassio-Bichloride of Plat Platinum and Chloride of Potassium) in Alcoh

a. In absence of free Hydrochloric Acid.

α. An excess of perfectly pure, recently precipita of platinum was digested for 6 days at from 59° to 97·5 per cent., in a stoppered bottle, with frequent s 72·5 grammes of the perfectly colorless filtrate left platinum dish, a residue which, dried at 212° F., The solution of 1 part of potassio-bichloride of pla fore 12,083 parts of alcohol of 97·5 per cent.

β. The same experiment was made with spirit o The filtrate was nearly colorless; upon evaporati ensued, on which account the residue was determin grammes yielded 0·008 grm. of platinum, correspon the potassio-bichloride. One part of the latter salt in 3,775 parts of spirit of wine of 76 per cent.

γ. The same experiment was made with spirit of the filtrate was distinctly yellowish. 63·2 grammes platinum, corresponding to 0·06 grm. of the potassio of this latter salt dissolves accordingly in 1,053 part 55 per cent.

b. In presence of free Hydrochloric Acid.

Recently precipitated potassio-bichloride of platin with spirit of wine of 76 per cent., to which some hydrochloric acid had been added. The solution was yellowish; 67 grammes left 0·0146 grm. of platinum, which corresponds to 0·0365 grm. of the potassio-bichloride. One part of the latter salt dissolves accordingly in 1,835 parts of spirit of wine of 76 per cent., mixed with hydrochloric acid.

9. SULPHATE OF SODA AND ALCOHOL (to § 69 *a*).

Experiments made with pure anhydrous sulphate of soda, in the manner described in 6, showed that this salt comports itself both with pure alcohol, and with alcohol containing sulphuric acid, exactly like the sulphate of potassa.

10. DEPORTMENT OF IGNITED SULPHATE OF SODA IN THE AIR (to § 69, *a*).

2·5169 grammes of anhydrous sulphate of soda were exposed, in a watch-glass, to the open air on a hot summer day. The first few minutes passed without any increase of weight, but after the lapse of 5 hours there was an increase of 0·0061 grm.

11. EXPERIMENTS WITH NITRATE OF SODA (to § 69, *b*).

a. 4·5479 grammes of pure nitrate of soda were exposed, in a state of fusion, to the air (in April, in fine weather); after the lapse of 24 hours, there was an increase of weight of 0·0006 grm.

b. 4·5479 grammes of pure nitrate of soda were dissolved in water, in a platinum dish, and pure nitric acid added to the solution; the mixture was then evaporated to dryness on the water-bath, and the residue cautiously heated until the mass at the bottom of the dish began to fuse. The contents of the dish weighed, after cooling, 4·5503 grammes. It was then again heated to complete fusion, and when cold it weighed 4·5474 grammes.

12. DEPORTMENT OF CHLORIDE OF SODIUM IN THE AIR (to § 69, *c*).

4·3281 grammes of chemically pure, intensely ignited (but not fused) chloride of sodium, which had been cooled under a bell-glass over sulphuric acid, acquired during 45 minutes' exposure to the (somewhat moist) air, an increase of weight of 0·0009 grm.

13. DEPORTMENT OF CHLORIDE OF SODIUM UPON IGNITION BOTH WITH AND WITHOUT CHLORIDE OF AMMONIUM (to § 69, *c*).

4·3281 grammes of chemically pure, ignited chloride of sodium were dissolved in water, in a moderate-sized platinum dish, and pure chloride of ammonium was added to the solution, which was then evaporated and the residue gently heated until the evolution of chloride of ammonium fumes had apparently ceased. The residue weighed 4·3334 grammes. It was then very gently ignited for about 2 minutes, and after this reweighed, when the weight was found to be 4·3314 grammes. A few minutes' ignition at a red heat reduced the weight to 4·3275 grammes, and 2 minutes' further ignition at a bright red heat (upon which occasion white fumes were seen to escape), to 4·3249 grammes.

14. DEPORTMENT OF CHLORIDE OF AMMONIUM UPON EVAPORATION AND DRYING (to § 70, *a*).

0·5625 gramme of pure and perfectly dry chloride of ammonium was dissolved in water, in a platinum dish, and the solution was evaporated to dryness on the water-bath; the weight was now found to be 0·5622 gramme (ratio 100 : 99·94). It was again heated for 15 minutes in the water-bath, and afterwards re-weighed, when the weight was found to be 0·5612 gramme (ratio 100 : 99·77). Exposed once more for 15 minutes to the same temperature, the residue weighed 0·5608 gramme (ratio 100 : 99·69).

15. SOLUBILITY OF AMMONIO-BICHLORIDE OF PLATINUM (BICHLORIDE OF PLATINUM AND CHLORIDE OF AMMONIUM) IN ALCOHOL (to § 70, *b*).

a. In absence of free Hydrochloric Acid.

α. An excess of perfectly pure, recently precipitated ammonio-bichloride of platinum was digested for 6 days, at 59°—68° F., with alcohol of 97·5 per cent., in a stoppered-bottle, the action of the alcohol being aided by frequent agitation.

74·3 grammes of the perfectly colorless filtrate left, upon evaporation in a platinum dish, a residue of platinum which, after ignition, weighed 0·0012 gramme, corresponding to 0·0028 of the ammonio-bichloride. One part of the latter salt dissolves accordingly in 26,535 parts of alcohol of 97·5 per cent.

β. The same experiment was made with spirit of wine of 76 per cent. The filtrate was distinctly yellowish.

81·75 grammes left 0·0257 gramme of platinum, which corresponds to 0·0584 gramme of the ammonio-bichloride. One part of the latter salt dissolves accordingly in 1,406 parts of spirit of wine of 76 per cent.

γ. The same experiment was made with spirit of wine of 55 per cent. The filtrate was distinctly yellow. Slight blackening ensued upon evaporation, and 56·5 grammes of the filtrate left 0·0364 gramme of platinum, which corresponds to 0·08272 gramme of the ammonio-bichloride. Consequently, 1 part of the latter salt dissolves in 665 parts of spirit of wine of 55 per cent.

b. In presence of Hydrochloric Acid.

The experiment described in *β* was repeated, with this modification, that some hydrochloric acid was added to the spirit of wine. 76·5 grms. left 0·0501 gramme of platinum, which corresponds to 0·1139 gramme of the ammonio-bichloride. 672 parts of the acidified alcohol had therefore dissolved 1 part of ammonio-bichloride of platinum.

16. SOLUBILITY OF CARBONATE OF BARYTA IN WATER (to § 71, *b*).

a. In Cold Water.—Perfectly pure, recently precipitated carbonate of baryta ($Ba\,O, C\,O_2$) was digested for 5 days with water of 60·8°—68° F., with frequent shaking of the mixture. The solution was filtered, and a portion of the filtrate tested with sulphuric acid, another portion with ammonia; the former re-agent immediately produced turbidity in the fluid, the latter only after the lapse of a considerable time. 84·82 grms. of the solution left, upon evaporation, 0·006 of $Ba\,O, C\,O_2$. One part of that salt dissolves consequently in 14,137 parts of cold water.

b. In Hot Water.—The same carbonate of baryta being boiled for 10 minutes with pure distilled water, gave a filtrate manifesting the same re-actions as that prepared with cold water, and remaining perfectly clear upon cooling. 84·82 grammes of the hot solution left, upon evaporation, 0·0055 grm. of carbonate of baryta. One part of that salt dissolves therefore in 15,421 parts of boiling water.

17. SOLUBILITY OF CARBONATE OF BARYTA IN WATER CONTAINING AMMONIA AND CARBONATE OF AMMONIA (to § 71, *b*).

A solution of chemically pure chloride of barium was mixed with am-

on ; the filtrate remained perfectly clear upon addition of sulphu
but after the lapse of a very considerable time, a hardly percep
cipitate separated. 84·82 grms. of the filtrate left, upon evapor
small platinum dish, and subsequent gentle ignition of the
0·0006 grm. of carbonate of baryta. One part of this salt had con
dissolved in 141,000 parts of the fluid.

18. SOLUBILITY OF SILICO-FLUORIDE OF BARIUM IN WATER (t

a. Recently precipitated, thoroughly washed silico-fluoride
was digested for 4 days in cold water, with frequent shaki
mixture; the fluid was then filtered off, and a portion of t
tested with dilute sulphuric acid, another portion with solution o
of lime; both re-agents produced turbidity, the former immed
latter after one or two seconds—precipitates separated from bot
after the lapse of some time. 84·82 grms. of the filtrate left
which, after being thoroughly dried, weighed 0·0223 gramm
part of the salt had consequently required 3,802 parts of cold
its solution.

b. Another sample of recently precipitated silico-fluoride of b
heated with water to boiling, and the solution allowed to
which a portion of the dissolved salt separated again). The
was left for a considerable time longer in contact with the u
salt, and was then filtered off. The filtrate showed the same d
with solution of sulphate of lime as that of *a.* 84·82 gramme
0·025 grm. of silico-fluoride of barium. One part of that salt h
ingly dissolved in 3,392 parts of water.

19. SOLUBILITY OF SILICO-FLUORIDE OF BARIUM IN WATER WITH HYDROCHLORIC ACID (to § 71, *c*).

a. Recently precipitated pure silico-fluoride of barium was d
3 weeks with cold water acidified with hydrochloric acid, the
action of the water being aided by frequent agitation of th
The filtrate gave with sulphuric acid a rather copious
84·82 grammes left 0·1155 gramme of thoroughly dried resid
calculated as silico-fluoride of barium, gives 733 parts of flu
of that salt.

b. Recently precipitated pure silico-fluoride of barium was
water very slightly acidified with hydrochloric acid, and t
heated to boiling. 84·82 grammes of the filtrate, cooled down
left a residue of 0·1322 gramme, which gives 640 parts of
part of the salt.

N.B. The solution of silico-fluoride of barium in hydrochl
not effected without decomposition; at least, the residue cont
after ignition, a rather large proportion of chloride of barium.

20. SOLUBILITY OF SULPHATE OF STRONTIA IN WATER (to §

a. In Water of 57·2° F.

84·82 grammes of a solution prepared by 4 days' digestion
precipitated sulphate of strontia with water at the common t
left 0·0123 grm. of sulphate of strontia. One part of Sr O, S
consequently in 6,895 parts of water.

of strontia. Consequently 1 part of $\mathrm{Sr\,O, S\,O_3}$ dis
boiling water.

21. SOLUBILITY OF SULPHATE OF STRONTIA I HYDROCHLORIC ACID AND SULPHURIC ACID (to § 7

a. 84·82 grammes of a solution prepared by
0·0077 grm. of $\mathrm{Sr\,O, S\,O_3}$.

b. 42·41 grammes of a solution prepared by
0·0036 grm.

c. Pure carbonate of strontia was dissolved in an
acid, and the solution precipitated with an excess
then allowed to stand in the cold for a fortnight.
filtrate left 0·0066 grm.

In *a.*	1 part of $\mathrm{Sr\,O, S\,O_3}$	required		11,
b.	1	„	„	11,
c.	1	„	„	12,
		Mean	. .	11,

22. SOLUBILITY OF SULPHATE OF STRONTIA IN HYDROCHLORIC ACID, AND ACETIC ACID (to § 72, *a*

a. Recently precipitated pure sulphate of stront
days in the cold with nitric acid of 4·8 per cent. 1
left 0·3451 grm. One part of the salt required ac
the dilute acid for its solution; in another experin
was found to require 429 parts of the dilute acid.

b. The same salt was digested for 2 days in the c
acid of 8·5 per cent. 100 grms. left 0·2115, and i
0·2104 grm. One part of the salt requires, accordi
of hydrochloric acid of 8·5 per cent. for its solution

c. The same salt was digested for 2 days in the
of 15·6 per cent. ($\bar{\mathrm{A}}$, H O). 100 grms. left 0·0126,
ment, 0·0129 grm. One part of the salt requir
7,843 parts of acetic acid of 15·6 per cent.

23. SOLUBILITY OF CARBONATE OF STRONTIA § 72, *b*).

Recently precipitated, thoroughly washed carbon
$\mathrm{C\,O_2}$) was digested several days with cold distilled
shaking. 84·82 grms. of the filtrate left, upon
weighing, after ignition, 0·0047 grm. One part of
requires therefore 18,045 parts of water for its solu

24. SOLUBILITY OF CARBONATE OF STRONTIA IN AMMONIA AND CARBONATE OF AMMONIA (to § 72, *b*)

Recently precipitated, thoroughly washed carbo
digested for four weeks with cold water containing a
of ammonia, the operation being aided by frequ
grammes of the filtrate left 0·0015 gramme of Sr O,
1 part of the salt requires 56,545 parts of this fluid

25. SOLUBILITY OF CARBONATE OF LIME IN COLD WATER (to § 73, *b*).

Recently precipitated carbonate of lime was boiled for some time with distilled water, and the fluid then digested for four weeks in the cold, with the undissolved residue; the operation being aided by frequent shaking. 84·82 grammes of the filtrate left 0·0080 of $Ca\,O, C\,O_2$. One part of the carbonate requires consequently 10,601 parts of cold water for its solution.

26. SOLUBILITY OF CARBONATE OF LIME IN BOILING WATER (to § 73, *b*).

Recently precipitated $Ca\,O, C\,O_2$ was boiled for some time with distilled water. 42·41 grammes of the filtrate left, upon evaporation and subsequent gentle ignition of the residue, 0·0048 gramme of $Ca\,O, C\,O_2$. The solution of 1 part of carbonate of lime requires consequently 8,834 parts of boiling water.

27. SOLUBILITY OF $Ca\,O, C\,O_2$ IN WATER CONTAINING AMMONIA AND CARBONATE OF AMMONIA (to § 73, *b*).

Pure dilute solution of chloride of calcium was precipitated with carbonate of ammonia and ammonia, and the precipitate allowed 24 hours to subside; the fluid was then filtered off. 84·82 grammes of the filtrate left 0·0013 grm. of $Ca\,O, C\,O_2$. One part of carbonate of lime requires consequently 65,246 parts of this fluid for its solution.

28. DEPORTMENT OF CARBONATE OF LIME UPON IGNITION IN A PLATINUM CRUCIBLE (to § 73, *b*.).

0·7955 grm. of perfectly dry carbonate of lime was exposed, in a small and thin platinum crucible, to the gradually increased, and finally most intense heat of a good *Berzelius*' lamp. The crucible was open and placed obliquely. After the first 15 minutes the mass weighed 0·6482 grm.,—after half an hour 0·6256 grm.,—after one hour 0·5927 grm., which latter weight remained unaltered after 15 minutes' additional heating. This corresponds to 74·5 per cent., whilst the proportion of lime in the carbonate is calculated at 56 per cent.; there remained therefore evidently still a considerable amount of the carbonic acid.

29. COMPOSITION OF OXALATE OF LIME DRIED AT 212° F. (to § 73, *c*).

0·8510 grm. of thoroughly dry pure carbonate of lime was dissolved in hydrochloric acid; the solution was precipitated with oxalate of ammonia and ammonia, and the precipitate collected upon a weighed filter and dried at 212° F., until the weight remained constant. The oxalate of lime so produced weighed 1·2461 grm. Calculating this as $Ca\,O, C_2O_3 + aq$, the amount found contained 0·4772 of $Ca\,O$, which corresponds to 56·07 per cent. in the carbonate of lime; the calculated proportion of lime in the latter is 56 per cent.

30. DEPORTMENT OF SULPHATE OF MAGNESIA IN THE AIR AND UPON IGNITION (to § 74, *a*).

0·8135 grm. of perfectly pure anhydrous $Mg\,O, S\,O_3$ in a covered pla-salt could not be accurately weighed, owing to weight.

0·8135 grm., exposed for some time to a very mod no diminution of weight; but after 5 minutes' exp heat, the substance was found to have lost 0·0075 g the residue in water gave no longer a clear fluid. A sulphate of magnesia, exposed in a small platinum minutes, to the heat of a powerful blast gas la hydrochloric acid, a solution in which chloride of duce the least turbidity.

31. SOLUBILITY OF THE BASIC PHOSPHATE AMMONIA IN PURE WATER (to § 74, *b*).

a. Recently precipitated basic phosphate of magn thoroughly washed with water, then digested for 2 about 59°, with frequent shaking.

84·42 grammes of the filtrate left . . of pyrophosphate of magnesia.

b. The same precipitate was digested in the same for 72 hours.

84·42 grammes of the filtrate left . .

which corresponds to 0·00552 grm. of the anhydro part of that salt dissolves therefore in 15,293 parts

The cold saturated solution gave, with ammoni short time, a distinctly perceptible crystalline precipi of phosphate of soda, it remained perfectly clear, an of two days no precipitate had formed;—phosphate produced a precipitate as large as that by ammonia.

32. SOLUBILITY OF BASIC PHOSPHATE OF MAG IN WATER CONTAINING AMMONIA (to § 74, *b*).

a. Pure basic phosphate of magnesia and ammoni least possible amount of nitric acid; a large quantit to the solution, then ammonia in excess. The mix stand at rest for 24 hours, then filtered; its tempe 84·42 grammes of the filtrate left 0·0015 grm. magnesia, which corresponds to 0·00184 grm. of tl salt. Consequently 1 part requires 45,880 parts o for its solution.

b. Pure basic phosphate of magnesia and ammo 4 weeks with ammoniated water, the operation bei shaking; the fluid (temperature 57·2° F.) was then grammes of the filtrate left 0·0024 grm. of pyroph which corresponds to 0·00296 grm. of the double s therefore dissolves in 42,780 parts of ammoniated average of *a* and *b*, 1 part of the double salt requi ammoniated water for its solution.

fully washed with water containing ammonia, was dissolved in water acidified with hydrochloric acid, ammonia added to the solution, and the fluid allowed to stand in the cold for 24 hours. 169·64 grammes of the filtrate left 0·0031 grm. of pyrophosphate of magnesia, corresponding to 0·0038 of anhydrous phosphate of magnesia and ammonia. One part of the double salt required therefore 44,600 parts of the fluid.

34. SOLUBILITY OF THE BASIC PHOSPHATE OF MAGNESIA AND AMMONIA IN WATER CONTAINING CHLORIDE OF AMMONIUM (to § 74, *b*).

Recently precipitated, thoroughly washed basic phosphate of magnesia and ammonia was digested in the cold with a solution of 1 part of chloride of ammonium in 5 parts of water. 18·4945 grammes of the filtrate left 0·002 grm. of pyrophosphate of magnesia, which corresponds to 0·00245 grm. of the double salt. One part of the salt dissolves therefore in 7,548 parts of the fluid.

35. SOLUBILITY OF THE BASIC PHOSPHATE OF MAGNESIA AND AMMONIA IN WATER CONTAINING AMMONIA AND CHLORIDE OF AMMONIUM (to § 74, *b*).

Recently precipitated, thoroughly washed phosphate of magnesia and ammonia was digested in the cold with a solution of 1 part of chloride of ammonium in 7 parts of ammoniated water. 23·1283 grammes of the filtrate left 0·0012 grm. of pyrophosphate of magnesia, which corresponds to 0·00148 grm. of the double salt. One part of the double salt requires consequently 15,627 part of the fluid for its solution.

36. DEPORTMENT OF ACID SOLUTIONS OF PYROPHOSPHATE OF MAGNESIA WITH AMMONIA (to § 74, *c*.).

0·3985 grm. of pyrophosphate of magnesia was treated for several hours, at a high temperature, with concentrated sulphuric acid. This exercised no perceptible action. It was only after the addition of some water that the salt dissolved. The fluid, heated for some time, gave, upon addition of ammonia in excess, a crystalline precipitate, which was filtered after 18 hours, the quantity of pyrophosphate of magnesia obtained was 0·3805 grm., that is 95·48 per cent. Phosphate of soda produced in the filtrate a trifling precipitate, which gave 0·0150 grm. of pyrophosphate of magnesia, that is 3·76 per cent.

0·3565 gramme of pyrophosphate of magnesia was dissolved in 3 grammes of nitric acid 1·2 of specific gravity; the solution was heated, diluted, and precipitated with ammonia: the quantity of pyrophosphate of magnesia re-precipitated amounted to 0·3485 grm., that is 98·42 per cent.; 0·4975 grm. was treated in the same manner with 7·6 grammes of the same nitric acid: the quantity re-obtained was 0·4935 grm., that is 99·19 per cent.

0·786 grm. treated in the same manner with 16·2 grammes of nitric acid, gave 0·7765 grm., that is 98·79 per cent.

to the $2MgO, PO_5$.	Re-obtained.
1 : 9	98·42
1 : 15	99·19
1 : 20	98·79

37. Solubility of pure Magnesia in Wate

a. In Cold Water.

Perfectly pure well crystallized sulphate of mag
water, and the solution precipitated with carbo
caustic ammonia; the precipitate was thorough
standing, it still retained a perceptible trace of
dissolved in pure nitric acid, carefully avoiding
The solution was then re-precipitated with carb
caustic ammonia, and the precipitate thoroughl
prepared perfectly pure basic carbonate of magn
platinum crucible until the weight remained const
pure magnesia was then digested in the cold for 24
water, the operation being aided by frequent shakin
used was perfectly free from chlorine, and left n
evaporation.

a. 84·82 grammes of the filtrate, cautiously eva
dish, left a residue weighing, after ignition, 0·0015
pure magnesia dissolved therefore in . . .
parts of cold water.

The digestion was continued for 48 hours longer

β. 84·82 grammes of the filtrate left 0·0016 g
part of the magnesia required therefore . .

γ. 84·82 grammes of the filtrate left 0·0015 g
part required . . . .

The solution of magnesia in cold water has
alkaline reaction, which is most easily perceived
of very faintly reddened tincture of litmus; the alk
solution is perfectly manifest also with slightly red
with turmeric or dahlia paper, if these test-papers
in contact with the solution.

Alkaline carbonates fail to render the solution t
ing. Phosphate of soda also fails to impair the cle
but if the fluid is mixed with a little ammonia a
becomes turbid, and deposits after some time a per
basic phosphate of magnesia and ammonia.

b. In Hot Water.

Upon boiling pure magnesia with water, a soluti
comports itself in every respect like the cold-
magnesia. A hot-prepared solution of magnesia do
upon cooling, nor does a cold-prepared solution
grammes of hot-prepared solution of magnesia left 0

gelatinous precipitates of hydrate of alumina. Upon further addition of ammonia in considerable excess, the precipitate redissolves gradually, but not completely.

b. If a drop of a dilute solution of alum is mixed with a copious amount of ammonia, and the mixture shaken, the solution appears almost perfectly clear; however, after standing at rest for some time, slight flakes separate.

c. If a solution of alumina, mixed with a large amount of ammonia, is filtered, and

α. The filtrate boiled for a considerable time, flakes of hydrate of alumina separate gradually in proportion as the excess of ammonia escapes.

β. The filtrate mixed with solution of chloride of ammonium, a very perceptible flocculent precipitate of hydrate of alumina separates immediately; the whole of the hydrated alumina present in the solution will thus separate if the chloride of ammonium be added in sufficient quantity.

γ. The filtrate mixed with sesquicarbonate of ammonia, the same reaction takes place as in *β*.

δ. The filtrate mixed with solution of chloride of sodium or chloride of potassium, no precipitate separates, but, after several days' standing, slight flakes of hydrate of alumina subside, owing to the decrease of ammonia by evaporation.

d. If a neutral solution of alumina is precipitated with carbonate of ammonia, or a strongly acidified (with hydrochloric or nitric acid) solution with pure ammonia; or if to a neutral solution a sufficient amount of chloride of ammonium is added besides the ammonia—even a considerable excess of the precipitants will fail to redissolve the precipitated alumina, as appears from the continued perfect clearness of the filtrates upon protracted boiling and evaporation.

39. PRECIPITATION OF ALUMINA BY SULPHIDE OF AMMONIUM (to § 75, *a*).

(*Experiments made by Mr. J. Fuchs, formerly Assistant in my Laboratory.*)

a. 50 c.c. of a solution of pure ammonia-alum, which contained 0·3939 of alumina, were mixed with 50 c.c. of water and 10 c.c. of solution of sulphide of ammonium, and the mixture was filtered after the lapse of ten minutes. The precipitate weighed, after ignition, 0·3825 grm.

b. The same experiment was repeated with 100 c.c. of water; the precipitate weighed 0·3759 grm.

c. The same experiment was repeated with 200 c.c. of water; the precipitated alumina weighed 0·3642 grm.

40. PRECIPITATION OF SESQUIOXIDE OF CHROMIUM BY AMMONIA (to § 76, *a*).

Solutions of sesquichloride of chromium and of chrome-alum (concentrated and dilute, neutral and acidified with hydrochloric acid) were mixed with ammonia in excess. All the filtrates drawn off immediately after precipitation appeared red, but when filtered after previous ebullition, they all appeared colorless, if the ebullition had been sufficiently protracted.

Perfectly pure, recently (hot) precipitated basic
gently heated with distilled water, and subseque
many weeks, the operation being aided by fre
clear solution gave no precipitate with sulphide of
after long standing.

84·82 grammes left 0·0014 grm. of oxide of zi
to 0·0019 of basic carbonate of zinc (Zn O assume
salt). One part of the basic carbonate requires
of water for solution.

42. DEPORTMENT OF SULPHIDE OF NICKEL W
AMMONIUM, ETC. (to § 79, *c*).

A dilute solution of pure sulphate of protoxide
was mixed with a very slight excess of colorless hyd
of ammonium perfectly saturated with sulphure
following experiments were then made with the pr

a. One portion was filtered off at once. The filtr
perfectly clear and colorless.

b. Another portion was digested with an excess
fectly saturated hydrosulphate of sulphide of ammo

α. Filtered without previous application of he
sented a hardly perceptible shade of yellow; no
even after long standing.

β. Filtered after previous application of heat.
hibited a more marked shade of yellow, and, after
deposited some sulphide of nickel.

c. Another portion was digested with an excess
ammonium (prepared by exposing perfectly satura
sulphide of ammonium to the action of the air). T
without the least shade of brown; after several d
precipitate of sulphide of nickel had separated.

d. Another portion was digested cold with am
filtrate exhibited a faint brownish tint.

e. Another portion was digested with ammonia a
phate of sulphide of ammonium. The filtrate w
brown color. After several days' standing, a slight
of nickel had separated.

f. Another portion was digested with ammonia a
ammonium. The filtrate was likewise of a brow
ported itself like the filtrate of *e.*

43. DEPORTMENT OF HYDRATE OF PROTOXIDE OF
BY ALKALIES (to § 80, *a*).

A solution of protochloride of cobalt was prec
solution of soda, and the precipitate washed with b
filtrate gave no longer the least indication of prese
dried and ignited residue, heated with water, ma
re-action. It was reduced by ignition in hydrogen
metallic cobalt digested hot with water. The deca
no alkaline re-action, even after considerable co

44. SOLUBILITY OF CARBONATE OF LEAD (to § 83, *a*).

a. In pure Water.

Recently precipitated and thoroughly washed pure carbonate of lead was digested for 8 days with water at the common temperature, the operation being aided by frequent shaking. 84·42 grammes of the filtrate were evaporated, some pure sulphuric acid being added during the process; the residuary sulphate of lead weighed 0·0019 grm., which corresponds to 0·00167 grm. of carbonate of lead. One part of the latter salt dissolves therefore in 50,551 parts of water. The solution, mixed with sulphuretted hydrogen water, remained perfectly colorless, not the least tint being detected in it, even upon looking through it from the top of the test cylinder.

b. In Water containing a little Acetate of Ammonia and also Carbonate of Ammonia and Ammonia.

A highly dilute solution of pure acetate of lead was mixed with carbonate of ammonia and ammonia in excess, and the mixture gently heated and then allowed to stand at rest for several days. 84·42 grammes of the filtrate left, upon evaporation with a little sulphuric acid, 0·0041 grm. of sulphate of lead, which corresponds to 0·0036 grm. of the carbonate. One part of the latter salt requires accordingly 23,450 parts of the fluid *b* for solution. The solution was mixed with sulphuretted hydrogen water; when looking through the fluid from the top of the test cylinder, a distinct coloration was visible; but when looking through the cylinder laterally, this coloration was hardly perceptible. Traces of sulphide of lead separated after the lapse of some time.

c. In Water containing a large Proportion of Nitrate of Ammonia, together with Carbonate of Ammonia and Caustic Ammonia.

A highly dilute solution of acetate of lead was mixed with nitric acid, then with carbonate of ammonia and caustic ammonia in excess; the mixture was gently heated, and allowed to stand at rest for 8 days. The filtrate, mixed with sulphuretted hydrogen, exhibited a very distinct brownish color upon looking through it from the top of the cylinder; but this color appeared very slight only when looking through the cylinder laterally. The amount of lead dissolved was unquestionably more considerable than the quantity dissolved in *b*.

45. SOLUBILITY OF OXALATE OF LEAD (to § 83, *b*)

A dilute solution of acetate of lead was precipitated with oxalate of ammonia and ammonia, the mixture allowed to stand at rest for some time, and then filtered. The filtrate, mixed with sulphuretted hydrogen, comported itself exactly like the filtrate of 44, *b*. The same deportment was observed in another similar experiment, in which nitrate of ammonia had been added to the solution.

46. SOLUBILITY OF SULPHATE OF LEAD IN PURE WATER (to § 83, *d*).

Thoroughly washed and still moist sulphate of lead was digested for 5 days with water, at a temperature of 50° to 59° F., the operation being aided by frequent shaking. 84·42 grammes of the filtrate (filtered off at 51·8° F.) left 0·0037 grm. of sulphate of lead. Consequently 1 part of this salt requires 22,816 parts of pure water of 51·8° F. for solution.

The solution, mixed with sulphuretted hydrogen, exhibited a distinct brown color when viewed from the top of the cylinder, but this color appeared very slight upon looking through the cylinder laterally.

47. SOLUBILITY OF SULPHATE OF LEAD IN WATER CONTAINING SULPHURIC ACID (to § 83, *d*).

A highly dilute solution of acetate of lead was mixed with an excess of dilute pure sulphuric acid; the mixture was very gently heated, and the precipitate allowed several days to subside. 80·31 grammes of the filtrate left 0·0022 grm. of sulphate of lead. One part of this salt dissolves therefore in 36,504 parts of water containing sulphuric acid. The solution, mixed with sulphuretted hydrogen, appeared colorless to the eye looking through the cylinder laterally, and very little darker when viewed from the top of the cylinder.

48. SOLUBILITY OF SULPHATE OF LEAD IN WATER CONTAINING AMMONIACAL SALTS AND FREE SULPHURIC ACID (to § 83, *d*).

A highly dilute solution of acetate of lead was mixed with a tolerably large amount of nitrate of ammonia, and sulphuric acid in excess added. After several days' standing, the mixture was filtered. The filtrate was nearly indifferent to sulphuretted hydrogen water; viewed from the top of the cylinder, it looked hardly perceptibly darker than pure water.

49. DEPORTMENT OF SULPHATE OF LEAD UPON IGNITION (to § 83, *d*).

Speaking of the determination of the atomic weight of sulphur, *Erdmann* and *Marchand* ("Journal für praktische Chemie," xxxi. 385) state that sulphate of lead loses some sulphuric acid upon ignition. To test the correctness of this statement, and to ascertain how far this loss might impair the accuracy of the method of determining lead as a sulphate, I heated 2·2151 grammes of absolutely pure PbO, SO_3 to the most intense redness, over a spirit-lamp with double draught. I could not perceive the slightest decrease in the weight of the ignited compound; at all events, the decrease did not amount to 0·0001 grm.

50. DEPORTMENT OF SOLUTIONS OF LEAD WITH SULPHURETTED HYDROGEN (to § 83, *f*).

It is a well-known fact that solutions of lead which contain much free acid are not precipitated by sulphuretted hydrogen unless diluted with water. *Triboulet* ("Archiv. der Pharmacie," xxix. 234) maintains that sulphuretted hydrogen fails to precipitate the whole of the lead from solutions of lead mixed with solution of acetate of potassa; but that the lead will completely precipitate if ammonia is added. To test the correctness of this statement, I added to a concentrated solution of acetate of potassa, mixed with a solution of neutral acetate of lead, and acidified with a drop of acetic acid, *a*, sulphuretted hydrogen water in excess; *b*, sulphuretted hydrogen gas in excess. In both cases, the precipitation was so complete that the filtrates, drawn off after vigorous agitation of the mixture, suffered not the least alteration upon addition of ammonia and sulphide of ammonium. It is *certain*, therefore, that *Triboulet's* statement is erroneous, and *probable* that this error was caused by the presence of iron in the fluid upon which this chemist operated.

51. DEPORTMENT OF METALLIC MERCURY AT THE COMMON TEMPERATURE AND UPON EBULLITION WITH WATER (to § 84, *a*).

To ascertain in what manner loss of metallic mercury occurs upon

I placed 6·4418 grammes of perfectly pure mercury upon a watch-glass, poured distilled water over the metal, removed the water again as far as practicable (by decantation and finally by means of blotting-paper), and weighed. I found the weight to be 6·4412 grammes, which, after several hours' exposure to the air, were reduced to 6·4411 grammes. I placed these 6·4411 grammes under a bell-jar over sulphuric acid, the temperature being about 62° or 63° F. After the lapse of 24 hours the weight had not altered in the least. I introduced the 6·4411 grammes of mercury into a flask, poured a copious quantity of distilled water over it, and strongly boiled the mixture for 15 minutes. I then placed the mercury again upon the watch-glass, dried it most carefully with blotting-paper, and weighed. The weight was now 6·4402 grammes. Finding that a trace of mercury had adhered to the paper, I repeated the same experiment with the 6·4402 grammes. After 15 minutes' boiling with water, the mercury had again lost 0·0004 grm. The remaining 6·4398 grammes were exposed to the air for 6 days (in summer, during very hot weather), after which they were found to have lost only 0·0005 grm.

52. Deportment of Sulphide of Mercury with Solution of Potassa, Sulphide of Ammonium, etc. (to § 84, *c*).

a. If recently precipitated pure sulphide of mercury is boiled with pure solution of potassa, not a trace of it dissolves in that fluid; hydrochloric acid produces no precipitate, nor even the least coloration, in the filtrate.

b. If sulphide of mercury is boiled with solution of potassa, with addition of some sulphuretted hydrogen water, sulphide of ammonium, or sulphur, complete solution is effected.

c. Digestion of sulphide of mercury with sulphide of ammonium (no matter whether colorless or yellow) fails to dissolve the least trace of the mercurial sulphide; cyanide of potassium also fails to dissolve it. Hydrochloric acid produced in the sulphide of ammonium filtrate a pure white turbidity or precipitate, and in the cyanide of potassium filtrate not the least turbidity.

d. Thoroughly washed sulphide of mercury, moistened with water, suffers no alteration upon exposure to the air; at least, the fluid which I obtained by washing sulphide of mercury which had been thus exposed to the air for 24 hours, did not manifest acid reaction, nor did it contain mercury or sulphuric acid.

53. Deportment of Oxide of Copper upon Ignition (to § 85, *b*).

Pure oxide of copper (prepared from nitrate of copper) was ignited in a platinum crucible, then cooled under a bell-jar over sulphuric acid, and finally weighed. The weight was 3·542 grammes. The oxide was then most intensely ignited for 5 minutes, over a *Berzelius'* lamp, cooled and re-weighed, when the weight was found unaltered; the oxide was then once more ignited for 5 minutes, but with the same result.

54. Deportment of Oxide of Copper in the Air (to § 85, *b*).

A platinum crucible containing 4·3921 grammes of gently ignited oxide of copper, prepared from the nitrate, was placed for 10 minutes, covered with the lid, in a warm room (in winter); the weight of the oxide of copper was found to have increased to 4·3939 grammes.

The oxide of copper was then intensely ignited over a spirit-lamp; after 10 minutes' standing in the covered crucible, the weight had not perceptibly increased; after 24 hours it had increased by 0·0036 grm.

55. DEPORTMENT OF SULPHIDE OF CADMIUM WITH AMMONIA, ETC. (to § 87, *c*).

Recently precipitated pure sulphide of cadmium was diffused through water, and the following experiments were made with the fluid.

a. A portion was digested cold with ammonia in excess, and the fluid filtered. The filtrate remained perfectly clear upon addition of hydrochloric acid.

b. Another portion was digested hot with excess of ammonia, and the fluid filtered. This filtrate likewise remained perfectly clear upon addition of hydrochloric acid.

c. Another portion was digested for some time with solution of cyanide of potassium, and the fluid filtered. This filtrate also remained perfectly clear upon addition of hydrochloric acid.

d. Another portion was digested with hydrosulphate of sulphide of ammonium, and the fluid filtered. The turbidity which hydrochloric acid imparted to this filtrate was pure white.

(A remark made by *Wackenroder*, in *Buchner's* "Repertorium der Pharmacie," xlvi. 226, induced me to make these experiments.)

56. DETERMINATION OF SODA IN SALTS WITH ORGANIC ACIDS (to § 98, 4).

1·154 grm. of paratartrate of soda gave, upon intense ignition, after deduction of 0·004 grm. of charcoal, 0·63 grm. of NaO, CO_2, which corresponds to 0·3698 of NaO = 32·05 per cent. (calculated 32·14 per cent.); this gives 99·7 instead of 100.

57. DETERMINATION OF BARYTA BY PRECIPITATION WITH CARBONATE OF AMMONIA (to § 101, 2, *a*).

0·7553 grm. of pure ignited chloride of barium was precipitated according to the directions of § 101, 2, *a*; the precipitate of BaO, CO_2 weighed 0·7142 grm., which corresponds to 0·554719 of BaO = 73·44 per cent. (100 parts of $BaCl$ ought to have given 73·59 parts). The result accordingly was 99·79 instead of 100.

58. DETERMINATION OF BARYTA IN ORGANIC SALTS (to § 101, 2, *b*).

0·686 grm. of paratartrate of baryta $[2 (BaO, \bar{R}) + 5\,aq]$, treated according to the directions of § 101, 2, *b*, gave 0·408 grm. of carbonate of baryta = 0·3169 of BaO = 46·20 per cent. (calculated 46·38 per cent.) which gives 99·61 instead of 100.

59. DETERMINATION OF STRONTIA AS SULPHATE OF STRONTIA (to § 102, 1, *a*).

a. An aqueous solution of 1·2398 grm. of $SrCl$ was precipitated with SO_3 in excess, and the precipitated sulphate of strontia washed with water. It weighed 1·4113 grm., which corresponds to 0·795408 grm. of SrO = 64·15 per cent. (calculated 65·38 per cent.); this gives 98·12 instead of 100.

Sr O = 68·68 per cent. (calculated 70·07 per cent.); this gives 98·02 instead of 100.

60. DETERMINATION OF STRONTIA AS SULPHATE, WITH CORRECTION (to § 102, 1).

The *filtrate* obtained in the experiment described 59, *b*, weighed 190·84 grammes. According to experiment No. 21, 11,862 parts of water containing sulphuric acid dissolve 1 part of sulphate of strontia. 190·84 grammes of the filtrate contain therefore 0·0161 grm. of that salt in solution. The *washing water* weighed 63·61 grammes. According to experiment No. 20, 6,895 parts of water dissolve 1 part of Sr O, S O$_3$; the 63·61 grammes of washing water contain therefore 0·0092 grm.

Adding 0·0161 and 0·0092 grm. to the 1·4024 grm. of precipitated sulphate of strontia, we find the total amount = 1·4277 grm., which corresponds to 0·80465 of Sr O = 69·91 per cent. in Sr O, C O$_2$ (calculated 70·07 per cent.); this gives 99·77 instead of 100.

61. DETERMINATION OF STRONTIA AS CARBONATE OF STRONTIA (to § 102, 2).

1·3104 of chloride of strontium, precipitated according to the directions of § 102, 2, gave 1·2204 grm. of Sr O, C O$_2$, containing 0·8551831 of Sr O = 65·26 per cent. (calculated 65·38), which gives 99·82 instead of 100.

62. DETERMINATION OF LIME AS SULPHATE OF LIME, BY PRECIPITATION (to § 103, 1, *a*).

(In the experiments Nos. 62 to 65, and No. 67, chemically pure air-dried carbonate of lime was used, in a portion of which the amount of anhydrous carbonate had been determined by very cautious heating. 0·7647 grm. of the heated carbonate left 0·7581 grm., which weight remained unaltered upon further (extremely gentle) ignition of the carbonate; the air-dried carbonate contains accordingly 55·516 per cent. of lime.)

1·186 grm. of the air-dried carbonate of lime was dissolved in hydrochloric acid, and the solution precipitated with sulphuric acid and alcohol (see § 103, 1, *a*). The precipitated sulphate of lime weighed 1·5949 grm., containing 0·65598 of Ca O = 55·31 per cent. calculated 55·51), which gives 99·64 instead of 100.

63. DETERMINATION OF Ca O AS Ca O, C O$_2$, BY PRECIPITATION WITH CARBONATE OF AMMONIA AND WASHING THE PRECIPITATE WITH PURE WATER (to § 103, 2, *a*).

A hydrochloric acid solution of 1·1437 grm. of the air-dried carbonate of lime of 62, gave upon precipitation with carbonate of ammonia (§ 103, 2, *a*), 1·1243 grm. of anhydrous carbonate of lime, corresponding to 0·629608 of Ca O = 55·05 per cent. (calculated 55·51 per cent.) which gives 99·17 instead of 100.

64. DETERMINATION OF Ca O AS Ca O, C O$_2$, BY PRECIPITATION WITH OXALATE OF AMMONIA FROM ALKALINE SOLUTION (to § 103, 2, *b*, *a*).

1·1734 grm. of the air-dried carbonate of lime of 62, dissolved in hydrochloric acid, and treated as stated § 103, 2, *b*, *a*, gave 1·1632 grm.

of CaO, CO_2 (re-action not alkaline), containing 0·651392 of CaO = 55·513 per cent. (calculated 55·516 per cent.), which gives 99·99 instead of 100.

65. Determination of Lime as Oxalate (to § 103, 2, *b*, *a*).

0·857 grm. of the air-dried carbonate of lime of 62 were dissolved in hydrochloric acid; the solution was precipitated with oxalate of ammonia and ammonia, the precipitate washed, and then dried at 212° F. until the weight remained constant. The precipitate ($CaO, \bar{O} + aq$) weighed 1·2461 grm., containing 0·477879 of CaO = 55·76 per cent. (calculated 55·516 per cent.), which gives 100·45 instead of 100.

66. Volumetrical Determination of Lime precipitated as Oxalate (to § 103, 2, *b*, *a*).

Six portions, of 10 c.c. each, were taken of a solution of pure chloride of calcium; in 2 portions the lime was determined in the gravimetrical way (by precipitation with oxalate of ammonia, and weighing as CaO, CO_2); in two by the alkalimetrical method, and in two by precipitation with oxalate of ammonia, and estimation of the oxalic acid in the precipitate by solution of permanganate of potassa. The following were the results obtained:—

a. In the gravimetrical way.	*b.* By the alkalimetrical method.	*c.* By solution of permanganate of potassa.
0·5617 CaO, CO_2	0·5614	0·5613
0·5620 „	0·5620	0·5620

67. Determination of CaO as CaO, CO_2 by Precipitation as $CaO, \bar{O}$ from Acid Solution (to § 103, 2, *b*, *β*).

0·857 grm. of the dry carbonate of lime of 62, dissolved in hydrochloric acid and precipitated from this solution according to the directions of § 103, 2, *b*, *β*, gave 0·8476 grm. of carbonate of lime (which did not manifest alkaline re-action, and the weight of which did not vary in the least upon evaporation with carbonate of ammonia), containing 0·474656 of CaO = 55·39 per cent. (calculated 55·51), which gives 99·78 instead of 100.

68. Determination of Magnesia as $2\,MgO, PO_5$ (to § 104, 2).

a. A solution of 1·0587 grm. of pure anhydrous sulphate of magnesia in water, precipitated according to § 104, 2, gave 0·9834 of pyrophosphate of magnesia, containing 0·3533944 of magnesia = 33·38 per cent. (calculated 33·35 per cent.), which gives 100·09 instead of 100.

b. 0·9672 grm. of sulphate of magnesia gave 0·8974 $2\,MgO, PO_5$ = 33·34 per cent. of MgO (calculated 33·35 per cent.), which gives 99·97 instead of 100.

69. Precipitation of Acetate of Zinc by Sulphuretted Hydrogen (to § 108, *b*).

a. A solution of pure acetate of zinc was treated with sulphuretted hydrogen in excess, the mixture allowed to stand at rest for some time, and then filtered. The filtrate was mixed with ammonia; it remained perfectly clear at first, and even after long standing a few hardly visible flakes only had separated.

b. A solution of acetate of zinc to which a tolerably large amount of

70. Determination of Mercury in the Metallic State, in the Humid Way, by Means of Protochloride of Tin (to § 118, 1, *b*).

2·01 grammes of chloride of mercury gave 1·465 grm. of metallic mercury = 72·88 per cent. (calculated 73·83 per cent.), which gives 98·71 instead of 100 (*Schaffner*).

71. Determination of Copper by Precipitation with Zinc in a Platinum Dish (to § 119, 2).

30·882 grammes of pure sulphate of copper were dissolved in water to 250 c.c. ; 10 c.c. of the solution contained accordingly 0·31387 grm. of metallic copper.

a. 10 c.c., precipitated with zinc in a platinum dish, gave 0·3140 = 100·06 instead of 100.

b. In a second experiment 10 c.c. gave 0·3138 = 100.

72. Determination of Copper as Sulpho-Subcyanide (to § 119, 3).

0·5965 grm. of pure sulphate of copper was dissolved in a little water, and, after addition of an excess of sulphurous acid, precipitated with sulphocyanide of potassium. The well-washed precipitate, dried at 212°F., weighed 0·2893, corresponding to 0·1892 $CuO = 31·72$ per cent. As sulphate of copper corresponds to 31·83 per cent., this gives 99·66 instead of 100.

73. Determination of Copper by De Haen's Method (to § 119, *c*).

Four portions, of 10 c.c. each, of a solution of sulphate of copper, containing 0·0254 grm. of metallic copper in 10 c.c. of solution, were severally mixed with iodide of potassium, then with 50 c.c. of a solution of sulphurous acid (50 c.c. coresponding to 12·94 c.c. of iodine solution). After addition of starch paste, iodine solution was added until the fluid appeared blue.

This required,—

In *a*, 4·09
b, 3·95
c, 4·06
d, 3·95

As 100 c.c. of iodine solution contained 0·58043 grm. of iodine, this gives—

For *a*, 0·0256 C uinstead of 0·0254
„ *b*, 0·0260 „ „
„ *c*, 0·0257 „ „
„ *d*, 0·0260 „ „

Another experiment, made with 100 c.c. of the same solution of sulphate of copper, gave 0·2606 instead of 0·254 of copper. Ammonia having been added to 10 c.c. of the solution of sulphate of copper, then hydrochloric acid in slight excess, 3·4 and 3·5 c.c. of iodine solution were required instead of 4 c.c.,—a proof that considerably more iodine had separated than corresponded to the oxide of copper.

74. ACTION OF SOLUTION OF CYANIDE OF POTASSIUM UPON AMMONIACAL SOLUTION OF OXIDE OF COPPER (to § 119, *d*).

Three portions, of 10 c.c. each, of a solution of sulphate of copper, containing 0·1 grm. of sulphate of copper in 10 c.c. of solution, were mixed with increasing quantities of solution of ammonia, and a sufficient amount of water to equalize the degree of concentration in the three portions. Solution of cyanide of potassium was then added, drop by drop, until the blue color had disappeared. This required the following quantities:—

Solution of sulphate of copper.	Solution of ammonia.	Water.	Solution of cyanide of potassium.
10 c.c.	4 c.c.	12	6·7
10 c.c.	8 c.c.	8	6·85
10 c.c.	16 c.c.	0	7·1

Neutral salts of ammonia also exercise some influence, as the following experiments show, which were made the next day with the same solutions:—

Solution of sulphate of copper.	Solution of ammonia.	Water, &c.	Solution of cyanide of potassium.
10 c.c.	2 c.c.	14 c.c.	6·70
10 c.c.	2 c.c.	14 c.c. solution of chloride of ammonium (1 : 10)	7·40
10 c.c.	6 c.c.	10 c.c. water 4 c.c. SO_3 dil. (1:5)	7·00
10 c.c.	2 c.c.	8 c.c. NH_4O, NO_5 (1:10) 6 c.c. water	7·30

75. PRECIPITATION OF NITRATE OF BISMUTH BY CARBONATE OF AMMONIA (to § 120, 1, *a*).

If a solution of nitrate of bismuth, no matter whether containing much or little free nitric acid, is mixed with water, precipitated with carbonate of ammonia and ammonia, and filtered without applying heat, the filtrate acquires, upon addition of sulphuretted hydrogen water, a blackish-brown color. But if the mixture before filtering is heated for a short time nearly to boiling, sulphuretted hydrogen fails to impart this color to the filtrate, or, at all events, the change of color is hardly visible to the eye looking through the full test-tube from the top.

76. DETERMINATION OF ANTIMONY AS SULPHIDE (to § 125, 1).

0·559 grm. of air-dried pure tartrate of antimony and potassa, treated according to the directions of § 125, 1, gave 0·2902 grm. of tersulphide of antimony, dried at 212° F., = 44·49 per cent. of teroxide of antimony. Heated to blackening in a current of carbonic acid, the precipitate lost 0·0079 grm., leaving accordingly 0·2823 grm. of anhydrous tersulphide of blackening, 99·77 instead of 100.

77. Deportment of a Hydrochloric Acid Solution of Teroxide of Antimony with Oxidizing Agents (to § 125, 3).

Three portions, of 10 c.c. each, of a solution of teroxide of antimony prepared with the least possible quantity of hydrochloric acid, and containing about 0·05 grm. of teroxide in 10 c.c. of solution, were mixed severally with 20 c.c. of hydrochloric acid, of 1·12 sp. gr., and different quantities of water; solution of permanganate of potassa was then added until the fluid appeared red.

Amount of water added.	Quantity of solution of permanganate of potassa used.
250 c.c.	16·2
400 c.c.	16·7
500 c.c.	17·95

10 c.c. of hydrochloric acid and 500 c.c. of water being added to 10 c.c. of the same solution of antimony, 22·6 c.c. of solution of permanganate of potassa were required. Bichromate of potassa exercised the same action upon hydrochloric acid solution of teroxide of antimony.

78. Volumetrical Determination of Antimony (to § 125, 3).

5·0822 grms. of chemically pure tartrate of antimony and potassa were dissolved to 250 c.c.

Four portions of this solution, of 10 c.c. each, were mixed severally with different quantities of a cold saturated solution of pure bicarbonate of soda, and with different quantities of water; after addition of 2 c.c. of starch paste to each portion, solution of iodine (100 c.c. = 0·53064 of iodine, corresponding to 0·30154 of teroxide of antimony) was dropped in until the iodide of starch reaction made its appearance in the several fluids.

1. 10 c.c. of the solution of tartrate of antimony and potassa + 5 c.c. of solution of $NaO, 2\,CO_2$; it took 29·9 c.c. of iodine solution to impart to the fluid a reddish color, which did not instantly disappear upon shaking; and 30·1 c.c. to produce a distinct blue tint; after some time, the latter also disappeared.

2. 10 c.c. of the tartar emetic solution + 10 c.c. of solution of $NaO, 2\,CO_2$. After addition of 29·2 c.c. of iodine solution, the fluid just began to exhibit a red tint, which immediately disappeared; 29·4 c.c. produced a distinct blue color, which disappeared only after 15 minutes.

3. 10 c.c. of the tartar emetic solution + 20 c.c. of solution of $NaO, 2\,CO_2$. After addition of 29·2 c.c. of iodine solution, the fluid just began to exhibit a red tint; 29·5 c.c. produced a distinct blue color, which disappeared only after 15 minutes.

4. 10 c.c. of tartar emetic solution + 20 c.c. of solution of $NaO, 2\,CO_2$ + 100 c.c. of water. The results obtained were exactly the same as in 3.

The results of the three last experiments, therefore, agreed very well, and as 29·5 c.c. of iodine solution correspond to 0·08895 of teroxide of antimony, which are contained in 0·20329 of tartrate of antimony and potassa, the two last experiments give 43·75 per cent. of teroxide of antimony in tartar emetic. The formula demands

(Sb = 120·2) 43·39. If the first reddening of the fluid which remains visible for a short time after stirring is considered as the final reaction, only 29·2 c.c. of iodine solution were required, which gives 43·31 of teroxide of antimony in tartar emetic.

79. ACTION OF IODINE SOLUTION UPON SOLUTION OF CARBONATE OF SODA (to § 125, 3).

A solution was used of pure carbonate of soda, perfectly free from reducing substances,* which contained 5 grammes of anhydrous salt in 100 c.c. of fluid. The iodine solution contained 0·53064 grm. of iodine in 100 c.c. of fluid. The temperature was 67·1° F. The quantity of starch paste added to each sample was 2 c.c. The two stages marked of the re-action were :—

a. The point at which the fluid just began to exhibit a faint blue tint.

b. The point at which the fluid presented the same blue color as a mixture of 30 c.c. of water with 2 c.c. of starch paste, and 1 drop of iodine solution.

Solution of NaO, CO_2	Water.	Solution of iodine used to produce the reaction.	
		a.	*b.*
1. 20 c.c.	0	0·2	0·4
2. 20 c.c.	60	0·55	0·8
3. 20 c.c.	120	0·8	1·2
4. 20 c.c.	280	1·7	2·2

Deducting for 1, 1 drop, for 2, 2 drops, for 3, 0·1 c.c., for 4, 0·2 c.c., of iodine solution, being the quantities severally required to impart a blue tint to pure water mixed with starch paste, the results of this series of experiments clearly show that the same quantity of carbonate of soda will prevent the larger amount of iodine from forming iodide of starch, the more considerable the volume of water present.

80. ACTION OF IODINE SOLUTION UPON SOLUTION OF BICARBONATE OF SODA (to § 125, 3).

The experiments were made with a cold saturated solution of the bicarbonate, free from simple carbonate of soda and from reducing agents; the other conditions were the same as in No. 79.

Solution of $NaO, 2CO_2$.	Water.	Solution of iodine used to produce the re-action.	
		a.	*b.*
1. 20 c.c.	0		1 drop
2. 20 c.c.	60	1 drop	0·05
3. 20 c.c.	120	0·05	0·10
4. 20 c.c.	280	0·10	0·25

The results of this series of experiments clearly show that bicarbonate of soda exercises no influence upon the iodide of starch re-action.

81. DETERMINATION OF ARSENIOUS ACID BY SOLUTION OF IODINE (to § 127, 5).

2·5 grammes of pure arsenious acid were dissolved in a solution of pure carbonate of soda, a very slight excess of hydrochloric acid was grm. of iodine in 100 c.c. of fluid.

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* Prepared from thoroughly washed bicarbonate of soda. A drop of a dilute solution of permanganate of potassa imparted to 20 c.c. of it a red tint, which did not disappear upon addition of dilute sulphuric acid in excess.

1. 10 c.c. of this solution + 20 c.c. of a solution of bicarbonate of soda saturated at 68° F. + 2 c.c. of starch paste. It took 49·05 c.c. of the iodine solution to impart a reddish tint to the fluid, which after a short time disappeared; and 49·25 c.c. to produce a distinct blue color.

2. Same conditions as in 1, but with addition of 250 c.c. of water; first appearance of a light bluish tint, after addition of 49·1 c.c. of the iodine solution; distinct blue color, after addition of 49·25 c.c.

3. Same conditions as in 1, simply substituting for 20 c.c. of solution of bicarbonate of soda, 10 c c. of solution of perfectly pure carbonate of soda (1 : 20), prepared from thoroughly washed bicarbonate. First, bluish tint, after addition of 49·25 c.c. of iodine solution; distinct blue color, after addition of 49·32 c.c.

4. Same conditions as in 3, with 20 c.c. of solution of carbonate of soda instead of 10 c.c. Distinct blue color, after addition of 49·27 c.c. of iodine solution.

5. Same conditions as in 4 + 250 c.c. of water. Distinct blue color, after addition of 49·3 c.c. of iodine solution.

6. Same conditions as in 5, with 50 c.c. of solution of carbonate of soda instead of 20 c.c. Distinct blue color, after addition of 49·46 c.c. of iodine solution.

These results are quite satisfactory. 49 c.c. of iodine solution were clearly sufficient to convert the arsenious into arsenic acid; they correspond to 0·1014 grm. of arsenious acid, whilst the 10 c.c. of solution used contain 0·1 grm.

82. Determination of Sulphuric Acid by Means of a Solution of Nitrate of Lead of known Strength (to § 132, I., 2, 3).

Grundmann.

1. 50 c.c. of water, mixed with a few drops of solution of iodide of potassium, required 0·15 of a solution of nitrate of lead, containing 165·57 grm. in 1 litre of fluid.

2. 50 c.c. of a solution of sulphate of potassa, containing 10 grm. of the salt in 1 litre of fluid, required, after addition of a few drops of solution of iodide of potassium, 5·85, 6·05, and 5·55 of the above solution of nitrate of lead, and accordingly, after deduction of 0·15 c.c., 5·7, 5·9, and 5·4, corresponding to 0·495, 0·513, and 0·470 of sulphate of potassa instead of 0·500.

3. To ascertain whether better results might be obtained by heating the solution of sulphate of potassa, the following experiments were made with the solution heated in the water-bath :—

a. 30 c.c. KO, SO_3 + 20 c.c. of water required 3·6 – 0·15 c.c. PbO, NO_5. which gives 0·3005 instead of 0·3 KO, SO_3.

b. 70 c.c. KO, SO_3 + 50 c.c. of water required 8·35 – 0·25 c.c PbO, NO_5, which gives 0·7055 instead of 0·700 KO, SO_3.

c. 10 c.c. KO, SO_3 + 40 c.c of water required 1·3 – 0·15 c.c. PbO, NO_5, which gives 0·1001 instead of 0·100 KO, SO_3.

83. Determination of Phosphoric Acid as Pyrophosphate of Magnesia (to § 134, *b*, *a*).

1·9159 and 2·0860 grms. of pure crystallized phosphate of soda, treated as directed § 134, *b*, *a*, gave 0·5941 and 0·6494 grm. of pyrophosphate of magnesia. This gives 19·83 and 19·91 per cent. of phosphoric acid in phosphate of soda, instead of 19·83 per cent.

84. DETERMINATION OF PHOSPHORIC ACID AS PHOSPHATE OF SESQUIOXIDE OF URANIUM (to § 134, *c*).

30 c.c. of a solution of pure phosphate of soda, treated with sulphate of magnesia, chloride of ammonium, and ammonia, as directed § 134, *b*, *a*, gave 0·3269 grm. of pyrophosphate of magnesia. 10 c.c. contained accordingly 0·06982 grm. of phosphoric acid.

10 c.c. of the same solution were then precipitated with acetate of sesquioxide of uranium as directed § 134, *c*. The ignited precipitate was treated with a little nitric acid, then again ignited; after cooling, it weighed 0·3478 gramme, corresponding to 0·06954 grm. of phosphoric acid.

85. INFLUENCE OF TEMPERATURE, ETC., UPON THE IODIDE OF STARCH RE-ACTION (to § 148, I., *a*).

See "Annal. d. Chem. u. Pharm.," 102, 186.

86. DETERMINATION OF FREE SULPHURETTED HYDROGEN BY MEANS OF SOLUTION OF IODINE (to § 148, I., *a*).

The experiments were made to settle the following questions:—

a. Does the quantity of iodine required remain the same for solutions of sulphuretted hydrogen of different degrees of dilution?

b. Does the formula $HS + I = HI + S$ really represent the decomposition which takes place, and may the method accordingly be considered to give correct results?

The sulphuretted hydrogen water was contained in a flask closed by a double-perforated cork; into one aperture a siphon tube with compression clamp was fitted, to draw off the fluid; into the other aperture a short open tube, which did not dip into the fluid.

Question *a*.

α. About 30 c.c. of iodine solution were introduced into a flask, which was then tared; sulphuretted hydrogen water was added until the yellow color had just disappeared. The flask was then closed, weighed, starch paste added, and then solution of iodine until the fluid appeared blue.

70·2 grms. of sulphuretted hydrogen water required 23·4 c.c. of iodine solution, 100 accordingly 33·33 c.c.—68·4 grms. required 22·7 c.c. of iodine solution, 100 accordingly 33·20 c.c.

β. Same process; but the solution of sulphuretted hydrogen was diluted with water free from air.

61·5 grms. of sulphuretted hydrogen water + 200 grms. of water required 20·7 c.c. of iodine solution, 100 accordingly 33·65 c.c.

52·4 grms. + 400 grms. of water required 17·7 c.c. of iodine solution, 100 accordingly 33·77.

The iodine solution contained 0·00498 of solution of iodine in 1 c.c. of fluid. Considering that addition of a larger volume of water necessarily involves a slight increase in the quantity of iodine solution, these results may be considered sufficiently corresponding.

Question *b*.

According to *a*, 100 grms. of HS water contained 0·02215 grm. of HS, assuming the proportion to be 100 : 33·2, 173·6 grms. of the same weighed 0·0920 grm., which corresponds to 0·03814 HS, or in per-cents, 0·02197; which resolves the second question also in the affirmative.

87. Determination of Nitric Acid by Pelouze's Method (to § 149, II., *a*, *a*).

See "Annal. d. Chem. u. Pharm.," 106, 217.

88. Determination of Nitric Acid by Stein's Method (to § 149, II., *b*).

1·0938 grm. of nitrate of potassa was treated as directed § 149, II., *b*. The arsenate of magnesia and ammonia, dried at 212° F., weighed 2·0528 grms., which give 1·0924 of nitrate of potassa = 99·87 instead of 100.

89. Solution of Chloride of Magnesium dissolves Oxalate of Lime (to § 154, 4).

If some chloride of calcium is added to a solution of chloride of magnesium, then a little oxalate of ammonia, no precipitate is formed at first; but upon slightly increasing the quantity of oxalate of ammonia, a trifling precipitate gradually separates after some time.

If an excess of oxalate of ammonia is added, the whole of the lime is thrown down, but the precipitate contains also oxalate of magnesia. This shows that to effect the separation of the two bases by oxalate of ammonia, the latter reagent must be added in excess; whilst, on the other hand, the operator must, in that case, be prepared to find oxalate of magnesia in the precipitated oxalate of lime, as the following experiments (No. 90) clearly show.

90. Experiments on the Separation of Lime from Magnesia (to § 154, 4).

The fluids employed in the following experiments were, a solution of chloride of calcium, 10 c.c. of which corresponded to 0·5618 CaO, CO_2; a solution of chloride of magnesium, containing 0·250 MgO in 10 c.c. of fluid; a solution of chloride of ammonium (1 : 8); solution of ammonia, containing 10 per cent. NH_3; a solution of 1 part of oxalate of ammonia in 24 parts of water; acetic acid, containing 30 per cent. $\bar{A}, HO$. The precipitation was effected at the common temperature; the precipitate of oxalate of lime was filtered off after 20 hours.

a. Influence of the degree of dilution.

a, 10 c.c. $MgCl$, 10 c.c. $CaCl$, 10 c.c. NH_4Cl, 4 drops NH_4O, 50 c.c. of water, 20 c.c. $NH_4O, \bar{O}$. Result, 0·5705 CaO, CO_2.

β. Same as *a*, with 150 c.c. of water instead of 50 c.c. Result, 0·5670 CaO, CO_2.

b. Influence of excess of ammonia.

Same as *a*, *β*, + 10 c.c. NH_4O. Result, 0·5614 grm. CaO, CO_2.

c. Influence of excess of chloride of ammonium.

Same as *a*, *β* + 40 c.c. NH_4Cl. Result, 0·5652 grm.

d. Influence of excess of ammonia and chloride of ammonium.

Same as *a*, *β*, + 30 c.c. NH_4Cl + 10 c.c. NH_4O. Result, 0·5613 grm.

e. Influence of free acetic acid.

Same as α, β, + 4 drops NH_4O + 6 drops $\bar{A}$. Result, 0·5594 grm.

f. Influence of excess of oxalate of ammonia, in feebly alkaline solution.

Same as α, β, + 20 c.c. $NH_4O, \bar{O}$. Result, 0·5644 grm. CaO, CO_2.

g. Influence of excess of oxalate of ammonia, in strongly alkaline solution.

Same as in α, β, + 10 c.c. NH_4O + 20 c.c. $NH_4O, \bar{O}$. Result, 0·5644 grm.

h. Influence of excess of oxalate of ammonia, in presence of much NH_4Cl and NH_4O.

Same as α, β, + 10 NH_4O + 30 NH_4Cl + 20 $NH_4O, \bar{O}$. Result, 0·5709 grm.

i. Influence of excess of oxalate of ammonia, in solution slightly acidified with $\bar{A}$.

Same as α, β,–4 drops NH_4O + 6 drops $\bar{A}$ + 20 c.c. $NH_4O, \bar{O}$. Result, 0·5661 grm.;
which proves that in presence of a notable amount of magnesia there is always a chance of oxalate of magnesia, or oxalate of magnesia and ammonia precipitating along with the oxalate of lime.

Another series of experiments made with a solution of oxalate of magnesia in hydrochloric acid to which ammonia in excess was added, proved also that, in presence of a notable quantity of magnesia, oxalate of magnesia, or oxalate of magnesia and ammonia, will always separate after standing for some time, no matter whether in a cold or a warm place.

In a third series of experiments, the lime was separated from the magnesia by double precipitation, in strict accordance with the instructions given in § 154 [30]. The same solutions were employed as in the first series, with the exception of the chloride of magnesium, for which a solution was substituted containing 0·2182 grm. MgO, in 10 c.c. of fluid.

10 c.c. $CaCl$ + 30 c.c. $MgCl$, + 20 c.c. NH_4Cl, + 300 c.c. water, + 6 drops ammonia, + a sufficient excess of oxalate of ammonia. Results, in two experiments, 0·5621 and 0·5652, mean 0·5636, instead of 0·5618 CaO, CO_2; in two other experiments, 0·6660 and 0·6489 MgO, mean 0·6574, instead of 0·6546.

91. SEPARATION OF COPPER AND CADMIUM FROM ZINC (to § 162, A, β).

See "Jour. f. prakt. Chem.," 73,241.

92. SEPARATION OF IODINE FROM CHLORINE BY PISANI'S METHOD (to § 169, [225]).

0·2338 grm. of iodide of potassium, dissolved in water, + ½ c.c. of solution of iodide of starch, required 14 c.c. of decimal standard solution of nitrate of silver = 0·2322 grm. of iodide of potassium.

0·3025 grm. of iodide of potassium, mixed with about double the quantity of chloride of sodium, required 18·2 c.c. of the silver solution = 0·3021 KI.

0·2266 grm. of iodide of potassium, mixed with about 100 times as much chloride of sodium, required 13·7 c.c. of the silver solution = 0·2272 KI.

93. SEPARATION OF IODINE FROM BROMINE, BY PISANI'S METHOD (to § 169, [229]).

0·3198 grm. of iodide of potassium, mixed with double the quantity of

94. Action of Sulphuretted Hydrogen upon various M Solutions—Sensibility of the Re-action (to § 208, 9).

To five portions, of 500 c.c. each, of a highly dilute aqueous of sulphuretted hydrogen, containing 0·003 H S in 1000 parts was added, to,

a. Cu Cl, which imparted a blackish color to the fluid.

b. As O_3, dissolved in H Cl, which produced a precipitate o 12 hours; the fluid had not quite cleared at the time.

c. Cd Cl, which gave a fine flocculent precipitate after 1 hour

d. Ag O, N O_5. The fluid appeared blackish; it required 12 the precipitate to subside completely.

e. Hg Cy. The fluid appeared blackish; it required 12 hou precipitate to subside.

95. Determination of Sulphuretted Hydrogen by Sol Cadmium (to § 208, 9).

230·3 grammes of the same sulphuretted hydrogen water served for the experiments No. 86, and contained in 100 0·02215 H S, were mixed with solution of cadmium in exces after 24 hours, and the precipitate washed, dried at 212° weighed. Result, 0·2395. If the precipitate had consisted sulphide of cadmium, it would have given, by calculation, 0·0247 H S, consequently too much. A portion of it was therefore d with carbonate of soda and nitrate of potassa, and the residue chlorine. Distinct re-action was observed.

96. Chlorimetrical Experiments (to § 224, sqq.)

10 grammes of chloride of lime were triturated with wat litre of fluid, with which the following experiments were made

a. Examination by *Gay-Lussac's* method (§ 226); result 23·52 per cent.

b. Examination by *Penot's* method (§ 227); result, 23·5—23·

c. Examination by means of iron (§ 228, modification *a* 23·6 per cent.

d. Examination by *Bunsen's* method (§ 228, D); result, 2 per cent.

97. Drying of Manganese Ores (to 229, I.).

Four small pans, I.—IV., containing each 8 grammes of m ore of 53 per cent., were first dried in the water-bath. After I. had lost 0·145; after 6 hours, II. 0·15; after 9 hours, I after 12 hours, IV. 0·15 grm. I. and II. having been left loosely covered, in the room for 12 hours, II. was found to weig as much as at first; I. wanted only 0·01 grm. of the original w

The four pans were now heated for 2 hours to 248° F. Afte they were found to have lost each 0·180 of the original weight II. having been left standing, loosely covered, in the room for were found to have again acquired their original weight by moisture. III. and IV. were heated for 2 hours to 302° F. 0·215 grm. Having been left standing, loosely covered, in the 72 hours, both were found to weigh 0·05 less than at first.

the hygroscopic moisture expelled to be re-absorbed by standing in the air, this shows that at 302° F. a little chemically combined water escapes along with the moisture, and, accordingly, that, in the drying of manganese ores, the temperature must not exceed 248° F. See also *Dingler's* "Polyt. Journ.," 135, 277 sqq.

98. Comparative Determinations of Manganese (to § 230).

A sample of manganese was dried at 212° F., and most carefully analysed, twice according to § 230, A, and twice according to § 230, C.

The former method gave 61·33 and 61·42, the latter 61·45 and 61·33 per cent.

99. Determination of Silver in Argentiferous Lead [to § 243, 1 (*Production of the Bead*), and § 243, 1 (*Determination of Silver in the Bead*), *a*].

a. 10 grammes of sulphide of lead and 0·3 grm. of sulphide of silver were treated as directed § 243, 1, and the silver in the bead determined as directed § 243, 1 (*Determination of Silver in the Bead*), *a.* Result, 8·093 grammes of bead, and from this, 0·3458 grm. of chloride of silver instead of 0·347 grm.

b. 5 grammes of sulphide of lead and 0·05 grm. of sulphide of silver gave 4·025 grms. of bead, and 0·0562 grm. of chloride of silver instead of 0·0578.

c. 10 grammes of sulphide of lead and 0·01 grm. of sulphide of silver gave 7·7384 grms. of bead, and 0·0106 grm. of chloride of silver instead of 0·0115 grm.

100. Volumetrical Determination of Zinc by Schaffner's Method (to § 245, *b*, 2).

An ammoniacal solution of 2·1081 grms. of oxide of zinc was prepared as directed § 245, *a*, and diluted to 500 c.c.

a. 50 c.c. of this solution, mixed first with 4, then with 2 additional drops of solution of sesquichloride of iron, required 25·3 c.c. of solution of sulphide of sodium. 6 drops of solution of sesquichloride of iron in 75 c.c. of ammoniated water, required 1·5 c.c. of solution of sulphide of sodium to produce a distinct color; this leaves accordingly for the zinc solution, 25·3—1·5 = 23·8.

b. 30 c.c., treated in the same way, required 15·3 (corrected).
c. 25 c.c. „ „ „ „ 13·1 „

According to *a*, 100 c.c. of zinc solution require 47·6 c.c. of solution of sulphide of sodm.
„ *b*, „ „ „ „ 51·0 „ „
„ *c*, „ „ „ „ 52·4 „ „

ADDENDUM.

DETERMINATION OF ANTIMONY AND SEPARATION OF A
ANTIMONY AND TIN.—*Bunsen* (" Annal. d. Chem. u. Phar

a. DETERMINATION OF ANTIMONY.

Bunsen recommends to weigh the antimony as antimona
of antimony ($Sb\ O_4$), and gives two methods by which the
tersulphide of antimony—the form in which antimony is u
tated in analysis—into antimonate of teroxide of antin
effected.

a. Moisten the dry tersulphide of antimony with a few c
acid of 1·42 sp. gr., then treat, in a weighed porcelain
concave lid, with 8—10 times the quantity of fuming nitric
the acid gradually evaporate on the water-bath. The sulphu
first as a fine powder, which, however, is readily and compl
during the process of evaporation. The white residual
crucible consists of antimonic acid and sulphuric acid,
ignition be converted, without loss, into antimonate of ter
mony. If the tersulphide of antimony contains a large
sulphur, this must first be removed by washing with bisulp
(see below), before proceeding to oxidation.

β. Mix the tersulphide of antimony with 30—50 times
of pure oxide of mercury,† and heat the mixture gradual
porcelain crucible. As soon as oxidation begins, which ma
the sudden evolution of gray mercurial fumes, moderate th
the evolution of mercurial fumes diminishes, raise the tem
always taking care, however, that no inflammable redu
brought into contact with the contents of the crucible. R
traces of oxide of mercury over the blast gas-lamp, tl
residual fine white powder of antimonate of teroxide of a
oxide of mercury generally leaves a trifling fixed residue
the amount of this should be determined once for all, the o
added approximately weighed, and the corresponding an
residue deducted from the antimonate of teroxide of a
volatilization of oxide of mercury proceeds much more
effected in a platinum crucible, instead of a porcelain c
platinum crucible is employed, it must be effectively prot
action of antimony upon it, by a *good lining* of oxide of

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* Nitric acid of 1·42 sp. gr. is not suitable for their purpose, as i
almost 18 degrees Fahrenheit above the fusing point of sulphur, whe
acid boils at 186·8° F., consequently below the fusing point of sulp
acid of 1·42 sp. gr., therefore, the separated sulphur fuses and fo
obstinately resist oxidation.

† The best way is to use oxide of mercury prepared in the humid w

‡ This is effected best, according to *Bunsen*, in the following
sealed end of a common test-tube before the glass-blower's lamp ; plac
in the centre of the platinum crucible, and blow into it, which will c
and assume the exact form of the interior of the crucible. Crack off
glass and smooth the sharp edge cautiously by fusion. A glass is thus
both ends, which exactly fits the crucible. To effect the lining by means
fill the crucible loosely with oxide of mercury up to the brim, th
gradually and slowly down to the bottom of the crucible, occasionall

the tersulphide of antimony contains free sulphur, this must first be removed by washing with bisulphide of carbon, before the oxidation can be proceeded with, since otherwise a slight deflagration is unavoidable. The bisulphide of carbon used may be very easily rectified, and then used again, so that the washing of a precipitate may be effected with as little as 10—15 grammes of bisulphide of carbon.

b. Separation of Arsenic from Antimony and Tin.

This new method is based upon the different deportment of the recently precipitated sulphides of these metals with bisulphite of potassa. If recently precipitated tersulphide of arsenic is digested with sulphurous acid and bisulphite of potassa, the precipitate is dissolved; upon boiling, the fluid becomes turbid, owing to the separation of sulphur, of which the greater part, however, disappears upon continued boiling. After the expulsion of the sulphurous acid, the fluid contains arsenite and hyposulphite of potassa $[2\,As\,S_3 + 8\,(K\,O,\,2\,SO_2) = 2\,(K\,O,\,As\,O_3) + 6\,(K\,O,\,S_2O_2) + S_3 + 7\,S\,O_2]$. Tersulphide of antimony and sulphide of tin do not show this re-action. They may, accordingly, both be separated from tersulphide of arsenic, simply by precipitating the solution of the three sulphides in sulphide of potassium, with a large excess of a solution of sulphurous acid in water, digesting the fluid for some time with the precipitate on the water-bath, and then boiling until about two-thirds of the water and the whole of the sulphurous acid are expelled. The residual tersulphide of antimony and sulphide of tin is free from arsenic, the filtrate containing the whole of the arsenic, which may be precipitated at once with sulphuretted hydrogen. To determine the arsenic, *Bunsen* oxidizes the dry tersulphide of arsenic, together with the filter, with *fuming* nitric acid, *gently* heats the slightly diluted solution with a little chlorate of potassa (to ensure the complete oxidation of the substances derived from the paper), and determines the arsenic finally as arsenate of magnesia and ammonia. In separating the sulphide of tin from the solution of arsenite of potassa, care must be taken to wash the sulphide of tin with concentrated solution of chloride of sodium, as the fluid runs turbid through the filter if pure water is used. As soon as the precipitate has been thoroughly washed with solution of chloride of sodium, the chloride of sodium adhering to the precipitate is removed by washing with a solution of acetate of ammonia containing a slight excess of acetic acid. The washings proceeding from this last operation must not be added to the chloride of sodium washings, as acetate of ammonia prevents the complete precipitation of arsenious acid by sulphuretted hydrogen.

Bunsen obtained very satisfactory results by this method.

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oxide of mercury from the interior of the glass. The inside of the crucible is thus covered with a layer of oxide of mercury ½ —1 line thick, which, after the removal of the glass, adheres with sufficient firmness, even upon ignition.

II. TABLES FOR THE CALCULATION OF ANALYSES.

TABLE I.

EQUIVALENTS OF THE ELEMENTS CONSIDERED IN THE PRESENT WORK.[*]

		O = 100.	H = 1.	
Aluminium	Al	170·42	13·63	(Berzelius)
Antimony	Sb	1503·80	120·30	(Schneider[†])
Arsenic	As	937·50	75·00	(Pelouze, Berzelius)
Barium	Ba	857·32	68·59	(Marignac)
Bismuth	Bi	2599·95	208·00	(Schneider)
Boron	B	138·05	11·04	(Berzelius)
Bromine	Br	999·62	79·97	(Marignac, revised by Berzelius)
Cadmium	Cd	700·00	56·00	(C. v. Hauer[‡])
Calcium	Ca	250·00	20·00	(Dumas; Erdmann and Marchand)
Carbon	C	75·00	6·00	,, ,,
Chlorine	Cl	443·28	35·46	(Marignac, revised by Berzelius)
Chromium	Cr	328·00	26·24[‖]	(Berlin, Peligot)
Cobalt	Co	375·00	30·00	(Schneider)
Copper	Cu	396·00	31·68	(Erdmann & Marchand)
Fluorine	Fl	237·50	19·00	(Louyet)
Gold	Au	2458·33	196·67	(Berzelius)
Hydrogen	H	12·50	1·00	(Dumas)
Iodine	I	1586·00	126·88	(Marignac, revised by Berzelius)
Iron	Fe	350·00	28·00	(Erdmann & Marchand)
Lead	Pb	1294·65	103·57	(Berzelius)
Lithium	Li	86·89	6·95	(Mallet)
Magnesium	Mg	150·19	12·00	(Marchand & Scheerer)
Manganese	Mn	344·68	27·57	(Berzelius)
Mercury	Hg	1250·60	100·05	(Erdmann & Marchand)
Molybdenum	Mo	575·00	46·00	(Berlin)

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[*] These equivalent numbers are derived from most careful and accurate investigations. Several of them differ from the numbers originally assumed, though not in consequence of recent direct experiments, but simply because they were originally derived from other equivalents which have since been corrected by more accurate investigations. It became necessary, therefore, to adjust the equivalents derived from the original numbers to the corrected numbers. For a detailed and very instructive statement of the various sources from which our present knowledge of the equivalents of the elements, &c., is derived, I refer to *A. Strecker's* paper on Atomic Weights in "Handwörterbuch der reinen u. angewandten Chemie," 2nd edit., vol. 2, 463.

[†] "Pogg. Annal.," 98, 293. *Schneider's* first experiments ("Journ. f. prakt. Chem., 68, 117) had given 1503, or 120·2, the numbers which I have still retained in § 90.

[‡] "Reports of Sittings of the Academy of Sciences at Vienna," XXV., 118.—I did not receive this most carefully determined equivalent number of cadmium in time to make use of it in the body of the present work. The old number (*Stromeyer's*), viz., 696·77, or 55·74, has accordingly been used in § 87.

[‖] In § 76, I have still retained the old equivalent of chromium, as determined by *Moberg*, *Lefort*, and *Wildenstein*, viz., 334·7, or 26·78. The number given in the table (328·00, or 26·24), which results from *Berlin's* corrections of *Lefort's* experiments ("Journ. f. prakt. Chem.," 71, 191), deserves, however, the preference.

		O = 100.	H = 1.	
Nickel	Ni	362·50	29·00	(Schneider)
Nitrogen	N	175·06	14·00	(Marignac, revised by Berzelius)
Oxygen	O	100·00	8·00	
Palladium	Pd	665·48	53·24	(Berzelius)
Phosphorus	P	387·50	31·00	(Schrötter)
Platinum	Pt	1236·75	98·94	(Andrews)
Potassium	K	488·86	39·11	(Marignac, revised by Berzelius)
Selenium	Se	493·75	39·5	(Berzelius, Saoc, Erdmann & Marchand—mean)
Silicon	Si	185·18*	14·81	(Berzelius)
Silver	Ag	1349·66	107·97	(Marignac, revised by Berzelius)
Sodium	Na	287·44	23·00	(Pelouze)
Strontium	Sr	545·93	43·67	(Stromeyer)
Sulphur	S	200·00	16·00	(Erdmann & Marchand)
Tin	Sn	725·00	58·00	(Mulder)
Titanium	Ti	312·50	25·00	(Pierre)
Uranium	Ur	742·87	59·40	(Ebelmen)
Zinc	Zn	406·59	32·53	(Axel Erdmann)

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* 185·18 is two-thirds of the number given by *Berzelius*, viz., 277·778, as I have regarded silicic acid as $Si\,O_2$.

TABLE II.

COMPOSITION OF THE BASES AND OXYGEN ACIDS.

a. BASES.

Group I.	Potassa	K	488·86	39·11	83·02
		O	100·00	8·00	16·98
		KO	588·86	47·11	100·00
...	Soda	Na	287·44	23·00	74·19
		O	100·00	8·00	25·81
		Na O	387·44	31·00	100·00
...	Lithia	Li	86·89	6·95	46·49
		O	100·00	8·00	53·51
		Li O	186·89	14·95	100·00
...	Oxide of Ammonium	NH_4	225·06	18·00	69·23
		O	100·00	8·00	30·77
		NH_4O	325·06	26·00	100·00
Group II.	Baryta	Ba	857·32	68·59	89·55
		O	100·00	8·00	10·45
		Ba O	957·32	76·59	100·00
...	Strontia	Sr	545·93	43·67	84·52
		O	100·00	8·00	15·48
		Sr O	645·93	51·67	100·00
...	Lime	Ca	250·00	20·00	71·43
		O	100·00	8·00	28·57
		Ca O	350·00	28·00	100·00
...	Magnesia	Mg	150·19	12·00	60·03
		O	100·00	8·00	39·97
		Mg O	250·19	20·00	100·00
Group III.	Alumina	Al_2	340·84	27·26	53·19
		O_3	300·00	24·00	46·81
		Al_2O_3	640·84	51·26	100·00

GROUP III.	Chromium, sesquioxide	Cr_2	656·00	52·48	68·62
		O_3	300·00	24·00	31·38
		Cr_2O_3	956·00	76·48	100·00
GROUP IV.	Zinc, oxide	Zn	406·59	32·53	80·26
		O	100·00	8·00	19·74
		ZnO	506·59	40·53	100·00
...	Manganese, protoxide	Mn	344·68	27·57	77·51
		O	100·00	8·00	22·49
		MnO	444·68	35·57	100·00
...	Manganese, sesquioxide	Mn_2	689·36	55·14	69·67
		O_3	300·00	24·00	30·33
		Mn_2O_3	989·36	79·14	100·00
...	Nickel, protoxide	Ni	362·50	29·00	78·38
		O	100·00	8·00	21·62
		NiO	462·50	37·00	100·00
...	Cobalt, protoxide	Co	375·00	30·00	78·95
		O	100·00	8·00	21·05
		CoO	475·00	38·00	100·00
...	Cobalt, sesquioxide	Co_2	750·00	60·00	71·43
		O_3	300·00	24·00	28·57
		Co_2O_3	1050·00	84·00	100·00
...	Iron, protoxide	Fe	350·00	28·00	77·78
		O	100·00	8·00	22·22
		FeO	450·00	36·00	100·00
...	Iron, sesquioxide	Fe_2	700·00	56·00	70·00
		O_3	300·00	24·00	30·00
		Fe_2O_3	1000·00	80·00	100·00
GROUP V.	Silver, oxide	Ag	1349·66	107·97	93·10
		O	100·00	8·00	6·90
		AgO	1449·66	115·97	100·00
...	Lead, oxide	Pb	1294·65	103·57	92·83
		O	100·00	8·00	7·17
		PbO	1394·65	111·57	100·00
...	Mercury, suboxide	Hg_2	2501·20	200·10	96·16
		O	100·00	8·00	3·84
		Hg_2O	2601·20	208·10	100·00

		O	100·00	8·00	7·41
		Hg O	1350·60	108·05	100·00
...	Copper, suboxide	Cu_2	792·00	63·36	88·79
		O	100·00	8·00	11·21
		Cu_2O	892·00	71·36	100·00
...	Copper, oxide	Cu	396·00	31·68	79·84
		O	100·00	8·00	20·16
		Cu O	496·00	39·68	100·00
...	Bismuth, oxide	Bi	2599·95	208·00	89·655
		O_3	300·00	24·00	10·345
		$Bi\ O_3$	2899·95	232·00	100·000
...	Cadmium, oxide	Cd	700·00	56·00	87·50
		O	100·00	8·00	12·50
		Cd O	800·00	64·00	100·00
GROUP VI.	Gold, teroxide	Au	2458·33	196·67	89·12
		O_3	300·00	24·00	10·88
		$Au\,O_3$	2758·33	220·67	100·00
...	Platinum, binoxide	Pt	1236·75	98·94	86·08
		O_2	200·00	16·00	13·92
		$Pt\ O_2$	1436·75	114·94	100·00
...	Antimony, teroxide	Sb	1503·80	120·30	83·37
		O_3	300·00	24·00	16·63
		$Sb\,O_3$	1803·80	144·30	100·00
...	Tin, protoxide	Sn	725·00	58·00	87·88
		O	100·00	8·00	12·12
		Sn O	825·00	66·00	100·00
...	Tin, binoxide	Sn	725·00	58·00	78·38
		O_2	200·00	16·00	21·62
		$Sn\ O_2$	925·00	74·00	100·00
...	Arsenious Acid	As	937·50	75·00	75·76
		O_3	300·00	24·00	24·24
		$As\,O_3$	1237·50	99·00	100·00

		AsO_5 . . 14

b. ACIDS.

...	Chromic acid	Cr . . . 3 O_3 . . . 3 CrO_3 . . 6
...	Sulphuric acid	S . . . 2 O_3 . . . 3 SO_3 . . 5
...	Phosphoric acid	P . . . 3 O_5 . . . 5 PO_5 . . 8
...	Boracic acid	B . . . 1 O_3 . . . 3 BO_3 . . 4
...	Oxalic acid	C_2 . . . 1 O_3 . . . 3 C_2O_3 . . 4
...	Carbonic acid	C . . . 7 O_2 . . . 2 CO_2 . . 27
...	Silicic acid	Si . . . 1 O_2 . . . 2 SiO_2 . . 3
...	Nitric acid	N . . . 17 O_5 . . . 5 NO_5 . . 67
...	Chloric acid	Cl . . . 44 O_5 . . . 5 ClO_5 . . 94

TABLE III.

FOR CALCULATING THE EQUIVALENT OF ONE OF THE CONSTITUENTS BY SIMPLE MULTIPLICATION OR DIVISION OF THE EQUIVALENT OF THE COMPOUND.

This Table contains only some of the more frequently occurring compounds; the formulæ preceded by ! give perfectly accurate results. The Table may also be extended to other compounds, by proceeding according to the instructions given in § 199.

FOR INORGANIC ANALYSIS.

CARBONIC ACID.

! Carbonate of lime × 0·44 = Carbonic acid.

CHLORINE.

Chloride of silver × 0·24724 = Chlorine.

COPPER.

Oxide of copper × 0·79839 = Copper.

IRON.

! Sesquioxide of iron × 0·7 = 2 Iron.
! Sesquioxide of iron × 0·9 = 2 Protoxide of iron.

LEAD.

Oxide of lead × 0·9283 = Lead.

MAGNESIA.

Pyrophosphate of magnesia × 0·36036 = 2 Magnesia.

MANGANESE.

Protosesquioxide of manganese × 0·72107 = 3 Manganese.
Protosesquioxide of manganese × 0·9303 = 3 Protoxide of manganese.

PHOSPHORIC ACID.

Pyrophosphate of magnesia × 0·6396 = Phosphoric acid.

$$\left.\begin{array}{l}\text{Phosphate of sesquioxide of uranium } (2\,Ur_2\,O_3\,PO_5) \times 0{\cdot}2 \\ \qquad\qquad\text{or} \\ \dfrac{\text{Phosphate of sesquioxide of uranium}}{5}\end{array}\right\} = \text{Phosphoric acid.}$$

POTASSA.

Chloride of potassium × 0·52445 = Potassium.
Sulphate of potassa × 0·5408 = Potassa.

$$\left.\begin{array}{l}\text{Potassio-bichloride of platinum} \times 0{\cdot}30507 \\ \qquad\qquad\text{or} \\ \dfrac{\text{Potassio-bichloride of platinum}}{3{\cdot}278}\end{array}\right\} = \text{Chloride of potassium.}$$

$$\left.\frac{\text{Potassio-bichloride of platinum}}{5{\cdot}188}\right\}$$

SODA.

Chloride of sodium × 0·5302 = Soda.
Sulphate of soda × 0·43658 = Soda.

SULPHUR.

Sulphate of baryta × 0·13724 = Sulphur.

SULPHURIC ACID.

Sulphate of baryta × 0·34309 = Sulphuric acid.

FOR ORGANIC ANALYSIS.

CARBON.

$$\left.\begin{array}{c}\text{Carbonic acid}\times 0{\cdot}2727\\ \text{or}\\ \dfrac{\text{Carbonic acid}}{3{\cdot}666}\\ \text{or}\\ \dfrac{\text{Carbonic acid}\times 3}{11}\end{array}\right\}=\text{Carbon.}$$

HYDROGEN.

$$\left.\begin{array}{c}\text{Water}\times 0{\cdot}1111\\ \text{or}\\ \dfrac{\text{Water}}{9}\end{array}\right\}=\text{Hydrogen.}$$

NITROGEN.

Ammonio-bichloride of platinum × 0·06271 = Nitrog
Platinum × 0·1415 = Nitrogen.

NUMBER OF THE COMPOUND

Elements.	Found.	Sought.	1
Aluminium	Alumina Al_2O_3	Aluminium Al_2	0·53186
Ammonium	Chloride of ammonium NH_4Cl	Ammonia NH_3	0·31804
	Ammonio-bichloride of platinum $NH_4Cl, PtCl_2$	Oxide of ammonium NH_4O	0·11644
	Ammonio-bichloride of platinum $NH_4Cl, PtCl_2$	Ammonia NH_3	0·07614
Antimony	Teroxide of antimony SbO_3	Antimony Sb	0·83368
	Tersulphide of antimony SbS_3	Antimony Sb	0·71479
	Tersulphide of antimony SbS_3	Teroxide of antimony SbO_3	0·85740
	Antimonious acid SbO_4	Teroxide of antimony SbO_3	0·94747
Arsenic	Arsenious acid AsO_3	Arsenic As	0·75758
	Arsenic acid AsO^5	Arsenic As	0·65217
	Arsenic acid AsO_5	Arsenious acid AsO_3	0·86087
	Tersulphide of arsenic AsS_3	Arsenious acid AsO_3	0·80488
	Tersulphide of arsenic AsS_3	Arsenic acid AsO_5	0·93496
	Arsenate of ammonia and magnesia $2MgO, NH_4O, AsO_5 + aq$	Arsenic acid AsO_5	0·60526
	Arsenate of ammonia and magnesia $2MgO, NH_4O, AsO_5 + aq$	Arsenious acid AsO_3	0·52105
Barium	Baryta BaO	Barium Ba	0·89554
	Sulphate of baryta BaO, SO_3	Baryta BaO	0·65690
	Carbonate of baryta BaO, CO_2	Baryta BaO	0·77684
	Silico-fluoride of barium $BaFl, SiFl_2$	Baryta BaO	0·54548
Bismuth	Teroxide of bismuth BiO_3	Bismuth Bi	0·89655
Boron	Boracic acid BO_3	Boron B	0·31515
Bromine	Bromide of silver AgBr	Bromine Br	0·42550
Cadmium	Oxide of cadmium CdO	Cadmium Cd	0·87500
Calcium	Lime CaO	Calcium Ca	0·71429
	Sulphate of lime CaO, SO_3	Lime CaO	0·41176

CONSTITUENT SOUGHT for every

FOUND, from 1—9.

2	3	4	5	6	
1·06373	1·59559	2·12746	2·65932	3·19118	3
0·63608	0·95413	1·27217	1·59021	1·90825	2
0·23288	0·34932	0·46576	0·58220	0·69864	0
0·15228	0·22842	0·30456	0·38070	0·45684	0
1·66736	2·50104	3·33472	4·16840	5·00208	5
1·42959	2·14438	2·85918	3·57397	4·28877	5
1·71480	2·57219	3·42959	4·28699	5·14439	6
1·89494	2·84242	3·78989	4·73736	5·68483	6
1·51516	2 27274	3·03032	3·78790	4·54548	5
1·30435	1·95652	2·60870	3·26087	3·91304	4
1·72174	2·58261	3·44348	4·30435	5·16521	6
1·60975	2·41463	3·21951	4·02439	4·82927	5
1·86992	2·80488	3·73984	4·67480	5·60975	6
1·21053	1·81579	2·42105	3·02631	3·63158	4·
1·04210	1·56316	2·08421	2·60526	3·12631	3·
1·79108	2·68662	3·58216	4·47770	5·37325	6·
1·31380	1·97070	2·62760	3·28450	3·94140	4·
1·55369	2·33053	3·10737	3·88421	4·66106	5·
1·09096	1·63644	2·18192	2·72740	3·27288	3·
1·79310	2·68965	3·58620	4·48275	5·37930	6·
0·63029	0·94544	1·26058	1·57573	1·89088	2·
0·85100	1·27650	1·70200	2·12750	2·55300	2·
1·75000	2·62500	3·50000	4·37500	5·25000	6·
1·42857	2·14286	2·85714	3·57143	4·28571	5·
0·82353	1·23529	1·64706	2·05882	2·47059	2·

Elements.	Found.	Sought.	1
Calcium	Carbonate of lime CaO, CO_2	Lime CaO	0·56000
Carbon	Carbonic acid CO_2	Carbon C	0·27273
	Carbonate of lime CaO, CO_2	Carbonic acid CO_2	0·44000
Chlorine	Chloride of silver $AgCl$	Chlorine Cl	0·24724
	Chloride of silver $AgCl$	Hydrochloric acid HCl	0·25421
Chromium	Sesquioxide of chromium Cr_2O_3	Chromium Cr_2	0·68619
	Sesquioxide of chromium Cr_2O_3	Chromic acid $2\,CrO_3$	1·31381
	Chromate of lead PbO, CrO_3	Chromic acid CrO_3	0·31049
Cobalt	Cobalt Co	Protoxide of cobalt CoO	1·26667
	Sulphate of protoxide of cobalt CoO, SO_3	Protoxide of cobalt CoO	0·48718
Copper	Oxide of copper CuO	Copper Cu	0·79839
	Subsulphide of copper Cu_2S	Copper Cu	0·79839
Fluorine	Fluoride of calcium $CaFl$	Fluorine Fl	0·48718
	Fluoride of silicon $SiFl_2$	Fluorine $2\,Fl$	0·71950
Hydrogen	Water HO	Hydrogen H	0·11111
Iodine	Iodide of silver AgI	Iodine I	0·54025
	Iodide of palladium PdI	Iodine I	0·70443
Iron	Sesquioxide of iron Fe_2O_3	Iron Fe_2	0·70000
	Sesquioxide of iron Fe_2O_3	Protoxide of iron $2\,FeO$	0·90000
Lead	Oxide of lead PbO	Lead Pb	0·92830
	Sulphate of lead PbO, SO_3	Oxide of lead PbO	0·73609
	Chloride of lead $PbCl$	Oxide of lead PbO	0·80248
	Chloride of lead $PbCl$	Lead Pb	0·74494
	Sulphide of lead PbS	Oxide of lead PbO	0·93309
Magnesium	Magnesia MgO	Magnesium Mg	0·60030
	Sulphate of magnesia MgO, SO_3	Magnesia MgO	0·33350
	Pyrophosphate of magnesia $2\,MgO, P_2O_5$	Magnesia $2\,MgO$	0·36036

2	3	4	5	6
1·12000	1·68000	2·24000	2·80000	3·36000
0·54546	0·81818	1·09091	1·36364	1·63636
0·88000	1·32000	1·76000	2·20000	2·64000
0·49448	0·74172	0·98896	1·23620	1·48344
0·50842	0·76263	1·01684	1·27105	1·52526
1·37238	2·05858	2·74477	3·43096	4·11715
2·62762	3·94142	5·25523	6·56904	7·88285
0·62097	0·93146	1·24195	1·55244	1·86293
2·53333	3·80000	5·06666	6·33333	7·60000
0·97436	1·46154	1·94872	2·43590	2·92308
1·59677	2·39516	3·19355	3·99193	4·79032
1·59677	2·39516	3·19355	3·99193	4·79032
0·97436	1·46154	1·94872	2·43590	2·92307
1·43900	2·15850	2·87800	3·59750	4·31700
0·22222	0·33333	0·44444	0·55555	0·66667
1·08050	1·62075	2·16100	2·70125	3·24150
1·40886	2·11329	2·81772	3·52215	4·22658
1·40000	2·10000	2·80000	3·50000	4·20000
1·80000	2·70000	3·60000	4·50000	5·40000
1·85660	2·78490	3·71320	4·64150	5·56980
1·47219	2·20829	2·94438	3·68048	4·41658
1·60495	2·40743	3·20990	4·01238	4·81486
1·48987	2·23480	2·97974	3·72468	4·46962
1·86619	2·79928	3·73238	4·66547	5·59856
1·20061	1·80091	2·40121	3·00151	3·60182
0·66700	1·00051	1·33401	1·66751	2·00101
0·72072	1·08108	1·44144	1·80180	2·16216

Elements.	Found.	Sought.	1
Manganese	Protoxide of manganese MnO	Manganese Mn	0·77512
	Protosesquioxide of manganese $MnO + Mn_2O_3$	Manganese Mn^3	0·72107
	Sesquioxide of manganese Mn_2O_3	Manganese Mn_2	0·69678
	Sulphate of protoxide of manganese MnO, SO_3	Protoxide of manganese MnO	0·47072
Mercury	Mercury Hg_2	Suboxide of mercury Hg_2O	1·03998
	Mercury Hg	Oxide of mercury HgO	1·07996
	Subchloride of mercury Hg_2Cl	Mercury Hg_2	0·84945
	Sulphide of mercury HgS	Mercury Hg	0·86213
Nickel	Protoxide of nickel NiO	Nickel Ni	0·78378
Nitrogen	Ammonio-bichloride of platinum $NH_4Cl, PtCl_2$	Nitrogen N	0·06071
	Platinum Pt	Nitrogen N	0·14155
	Sulphate of baryta BaO, SO_3	Nitric acid NO_5	0·46322
	Cyanide of silver Ag, C_2N	Cyanogen C_2N	0·19410
	Cyanide of silver Ag, C_2N	Hydrocyanic acid C_2N, H	0·20156
Oxygen	Alumina Al_2O_3	Oxygen O_3	0·46814
	Teroxide of antimony SbO_3	Oxygen O_3	0·16632
	Arsenious acid AsO_3	Oxygen O_3	0·24242
	Arsenic acid AsO_5	Oxygen O_5	0·34783
	Baryta BaO	Oxygen O	0·10446
	Oxide of lead PbO	Oxygen O	0·07170
	Oxide of cadmium CdO	Oxygen O	0·12500
	Lime CaO	Oxygen O	0·28571
	Sesquioxide of chromium Cr_2O_3	Oxygen O_3	0·31381
	Sesquioxide of iron Fe_2O_3	Oxygen O_3	0·30000
	Protoxide of iron FeO	Oxygen O	0·22222
	Potassa KO	Oxygen O	0·16982
	Silicic acid SiO_2	Oxygen O_2	0·51925

2	3	4	5	6	
1·55024	2·32536	3·10048	3·87560	4·65072	5·
1·44214	2·16321	2·88428	3·60535	4·32641	5·
1·39356	2·09034	2·78712	3·48390	4·18068	4·
0·94144	1·41217	1·88289	2·35361	2·82433	3·
2·07996	3·11994	4·15992	5·19990	6·23988	7·
2·15992	3·23988	4·31984	5·39980	6·47977	7·
1·69890	2·54836	3·39781	4·24726	5·09672	5·
1·72425	2·58638	3·44850	4·31063	5·17275	6·
1·56757	2·35135	3·13514	3·91892	4·70270	5·
0·12542	0·18812	0·25083	0·31354	0·37625	0·
0·28310	0·42464	0·56619	0·70774	0·84929	0·
0·92644	1·38966	1·85288	2·31610	2·77932	3·
0·38820	0·58230	0·77640	0·97050	1·16460	1·
0·40312	0·60468	0·80624	1·00780	1·20936	1·4
0·93627	1·40441	1·87254	2·34068	2·80882	3·
0·33264	0·49896	0·66528	0·83160	0·99792	1·1
0·48484	0·72726	0·96968	1·21210	1·45452	1·6
0·69565	1·04348	1·39130	1·73913	2·08696	2·4
0·20892	0·31338	0·41784	0·52230	0·62675	0·7
0·14340	0·21510	0·28680	0·35850	0·43020	0·5
0·25000	0·37500	0·50000	0·62500	0·75000	0·8
0·57143	0·85714	1·14286	1·42857	1·71429	2·0
0·62762	0·94143	1·25524	1·56905	1·88286	2·1
0·60000	0·90000	1·20000	1·50000	1·80000	2·1
0·44444	0·66667	0·88889	1·11111	1·33333	1·5
0·33964	0·50946	0·67928	0·84910	1·01892	1·1
1·03846	1·55769	2·07692	2·59615	3·11538	3·6

TABLE IV.

Elements.	Found.	Sought.	1
Oxygen	Protoxide of cobalt $Co\,O$	Oxygen O	0·21053
	Oxide of copper $Cu\,O$	Oxygen O	0·20161
	Magnesia $Mg\,O$	Oxygen O	0·39970
	Protoxide of manganese $Mn\,O$	Oxygen O	0·22488
	Protosesquioxide of manganese $Mn\,O + Mn_2\,O_3$	Oxygen O_4	0·27593
	Sesquioxide of manganese $Mn_2\,O_3$	Oxygen O_3	0·30322
	Soda $Na\,O$	Oxygen O	0·25810
	Protoxide of nickel $Ni\,O$	Oxygen O	0·21622
	Oxide of mercury $Hg\,O$	Oxygen O	0·07404
	Suboxide of mercury $Hg_2\,O$	Oxygen O	0·03844
	Oxide of silver $Ag\,O$	Oxygen O	0·06898
	Strontia $Sr\,O$	Oxygen O	0·15482
	Water $H\,O$	Oxygen O	0·88889
	Teroxide of bismuth $Bi\,O_3$	Oxygen O_3	0·18345
	Oxide of zinc $Zn\,O$	Oxygen O	0·19740
	Binoxide of tin $Sn\,O_2$	Oxygen O_2	0·21622
Phosphorus	Phosphoric acid $P\,O_5$	Phosphorus P	0·43662
	Pyrophosphate of magnesia $2\,Mg\,O, P\,O_5$	Phosphoric acid $P\,O_5$	0·63964
	Phosphate of sesquioxide of iron $Fe_2\,O_3, P\,O_5$	Phosphoric acid $P\,O_5$	0·47020
	Phosphate of silver $3\,Ag\,O, P\,O_5$	Phosphoric acid $P\,O_5$	0·16949
	Pyrophosphate of silver $2\,Ag\,O, P\,O_5$	Phosphoric acid $P\,O_5$	0·23437
Potassium	Potassa $K\,O$	Potassium K	0·83018
	Sulphate of potassa $K\,O, S\,O_3$	Potassa $K\,O$	0·54080
	Nitrate of potassa $K\,O, N\,O_5$	Potassa $K\,O$	0·46590
	Chloride of potassium $K\,Cl$	Potassium K	0·52445
	Chloride of potassium $K\,Cl$	Potassa $K\,O$	0·63173
	Potassio-bichloride of platinum $K\,Cl, Pt\,Cl_2$	Potassa $K\,O$	0·19272

2	3	4	5	6	
0·42106	0·63159	0·84212	1·05265	1·26318	
0·40323	0·60484	0·80645	1·00807	1·20968	1
0·79939	1·19909	1·59879	1·99849	2·39818	2
0·44976	0·67464	0·89952	1·12440	1·34928	1
0·55786	0·83679	1·11572	1·39465	1·67359	1
0·60644	0·90966	1·21288	1·51610	1·81932	2·
0·51621	0·77431	1·03242	1·29052	1·54863	1·
0·43244	0·64866	0·86488	1·08110	1·29732	1·
0·14808	0·22212	0·29616	0·37021	0·44425	0·
0·07688	0·11533	0·15377	0·19221	0·23066	0·
0·13796	0·20694	0·27592	0·34490	0·41388	0·4
0·30964	0·46446	0·61928	0·77410	0·92892	1·0
1·77778	2·66667	3·55556	4·44445	5·33333	6·2
0·20690	0·31035	0·41380	0·51725	0·62070	0·7
0·39480	0·59220	0·78960	0·98700	1·18440	1·3
0·43244	0·64866	0·86488	1·08110	1·29732	1·5
0·87324	1·30896	1·74648	2·18309	2·61971	3·0
1·27928	1·91982	2·55856	3·19820	3·83784	4·4
0·94040	1·41060	1·88080	2·35099	2·82119	3·2
0·33898	0·50847	0·67796	0·84745	1·01694	1·18
0·46874	0·70311	0·93748	1·17185	1·40622	1·64
1·66036	2·49054	3·32072	4·15090	4·98108	5·81
1·08161	1·62241	2·16321	2·70402	3·24482	3·78
0·93179	1·39769	1·86359	2·32949	2·79539	3·26
1·04890	1·57335	2·09780	2·62225	3·14669	3·6
1·26346	1·89519	2·52692	3·15865	3·79037	4·4
0·38545	0·57817	0·77090	0·96362	1·15634	1·3

II. X X

Elements.	Found.	Sought.	1
Potassium	Potassio-bichloride of platinum $KCl, PtCl_2$	Chloride of potassium KCl	0·30507
Silicon	Silicic acid SiO_2	Silicon Si	0·48077
Silver	Chloride of silver $AgCl$	Silver Ag	0·75276
	Chloride of silver $AgCl$	Oxide of silver AgO	0·80854
Sodium	Soda NaO	Sodium Na	0·74190
	Sulphate of soda NaO, SO_3	Soda NaO	0·43658
	Nitrate of soda NaO, NO_5	Soda NaO	0·36465
	Chloride of sodium $NaCl$	Soda NaO	0·53022
	Chloride of sodium $NaCl$	Sodium Na	0·39337
	Carbonate of soda NaO, CO_2	Soda NaO	0·58487
Strontium	Strontia SrO	Strontium Sr	0·84518
	Sulphate of strontia SrO, SO_3	Strontia SrO	0·56367
	Carbonate of strontia SrO, CO_2	Strontia SrO	0·70139
Sulphur	Sulphate of baryta BaO, SO_3	Sulphur S	0·13724
	Tersulphide of arsenic AsS_3	Sulphur S_3	0·39024
	Sulphate of baryta BaO, SO_3	Sulphuric acid SO_3	0·34309
Tin	Binoxide of tin SnO_2	Tin Sn	0·78378
	Binoxide of tin SnO_2	Protoxide of tin SnO	0·89189
Zinc	Oxide of zinc ZnO	Zinc Zn	0·80260

2	3	4	5	6	
0·61015	0·91522	1·22030	1·52537	1·83044	2
0·96154	1·44231	1·92308	2·40385	2·88462	3
1·50552	2·25828	3·01104	3·76380	4·51656	5
1·61708	2·42562	3·23416	4·04270	4·85124	5
1·48379	2·22569	2·96758	3·70948	4·45137	5
0·87316	1·30975	1·74633	2·18291	2·61949	3
0·72930	1·09395	1·45860	1·82325	2·18789	2
1·06043	1·59065	2·12086	2·65108	3·18130	3
0·78673	1·18009	1·57346	1·96683	2·36019	2
1·16974	1·75460	2·33947	2·92434	3·50921	4·
1·69036	2·53554	3·38072	4·22590	5·07108	5·
1·12734	1·69101	2·25469	2·81836	3·38204	3·
1·40278	2·10417	2·80556	3·50695	4·20834	4·
0·27447	0·41171	0·54894	0·68618	0·82342	0·
0·78049	1·17073	1·56097	1·95122	2·34146	2·
0·68619	1·02929	1·37238	1·71548	2·05857	2·
1·56757	2·35135	3·13514	3·91892	4·70270	5·
1·78378	2·67568	3·56757	4·45946	5·35135	6·
1·60520	2·40780	3·21040	4·01300	4·81560	5·

TABLE V.

SPECIFIC GRAVITY AND ABSOLUTE WEIGHT OF SEVERAL GASES.

	Specific gravity, atmospheric air = 1·0000.	1 litre (1000 cubic centimetres) of gas at 0° C. and 0·76 metre bar. pressure weighs grammes.
Atmospheric air	1·0000	1·29366
Oxygen	1·10832	1·43379
Hydrogen	0·06927	0·08961
Water, vapor of	0·62343	0·80651
Carbon, vapor of	0·83124	1·07534
Carbonic acid	1·52394	1·97146
Carbonic oxide	0·96978	1·25456
Marsh gas	0·55416	0·71689
Elayl gas	0·96978	1·25456
Phosphorus, vapor of	4·29474	5·55593
Sulphur, vapor of	6·64992	8·60273
Hydrosulphuric acid	1·17759	1·52340
Iodine, vapor of.	8·78898	113·6995
Bromine, vapor of	5·53952	7·16625
Chlorine	2·45631	3·17763
Nitrogen	0·96978	1·25456
Ammonia	0·58879	0·76169
Cyanogen	1·80102	2·32991

TABLE VI.

COMPARISON OF THE DEGREES OF THE MERCURIAL THERMOMETER WITH THOSE OF THE AIR THERMOMETER.

According to Dulong and Petit.

Degrees of the mercurial thermometer.	Degrees of the air thermometer.	Degrees of the mercurial thermometer.	Degrees of the air thermometer.
105	104·8	220	216·2
110	109·6	230	225·9
120	119·5	240	235·4
130	129·2	250	245·0
140	139·0	260	254·6
150	148·7	270	264·0
160	158·4	280	273·5
170	168·0	290	283·2
180	177·7	300	292·7
190	187·4	320	311·6
200	197·0	340	330·5
210	206·7	350	340·0

According to Magnus.

Degrees of the mercurial thermometer.	Degrees of the air thermometer.
100	100·00
150	148·74
200	197·49
250	245·39
300	294·51
330	320·92

According to Regnault.

Air thermometer.	Mercurial thermometer.
0	0
50	50·2
100	100·0
150	150·0
200	200·0
250	250·3
300	301·2
325	326·9
350	353·3

FOR THE CONVERSION OF DEGREES
INTO DEGREES OF

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
—50°	—58·0°	—3°	26·6°	44°	111·2°	91°	195·8°
—49	—56·2	—2	28·4	45	113·0	92	197·6
—48	—54·4	—1	30·2	46	114·8	93	199·4
—47	—52·6	0	32·0	47	116·6	94	201·2
—46	—50·8	+1	33·8	48	118·4	95	203·0
—45	—49·0	2	35·6	49	120·2	96	204·8
—44	—47·2	3	37·4	50	122·0	97	206·6
—43	—45·4	4	39·2	51	123·8	98	208·4
—42	—43·6	5	41·0	52	125·6	99	210·2
—41	—41·8	6	42·8	53	127·4	100	212·0
—40	—40·0	7	44·6	54	129·2	101	213·8
—39	—38·2	8	46·4	55	131·0	102	215·6
—38	—36·4	9	48·2	56	132·8	103	217·4
—37	—34·6	10	50·0	57	134·6	104	219·2
—36	—32·8	11	51·8	58	136·4	105	221·0
—35	—30·0	12	53·6	59	138·2	106	222·8
—34	—29·2	13	55·4	60	140·0	107	224·6
—33	—27·4	14	57·2	61	141·8	108	226·4
—32	—25·6	15	59·0	62	143·6	109	228·2
—31	—23·8	16	60·8	63	145·4	110	230·0
—30	—22·0	17	62·6	64	147·2	111	231·8
—29	—20·2	18	64·4	65	149·0	112	233·6
—28	—18·4	19	66·2	66	150·8	113	235·4
—27	—16·6	20	68·0	67	152·6	114	237·2
—26	—14·8	21	69·8	68	154·4	115	239·0
—25	—13·0	22	71·6	69	156·2	116	240·8
—24	—11·2	23	73·4	70	158·0	117	242·6
—23	— 9·4	24	75·2	71	159·8	118	244·4
—22	— 7·6	25	77·0	72	161·6	119	246·2
—21	— 5·8	26	78·8	73	163·4	120	248·0
—20	— 4·0	27	80·6	74	165·2	121	249·8
—19	— 2·2	28	82·4	75	167·0	122	251·6
—18	— 0·4	29	84·2	76	168·8	123	253·4
—17	+ 1·4	30	86·0	77	170·6	124	255·2
—16	3·2	31	87·8	78	172·4	125	257·0
—15	5·0	32	89·6	79	174·2	126	258·8
—14	6·8	33	91·4	80	176·0	127	260·6
—13	8·6	34	93·2	81	177·8	128	262·4
—12	10·4	35	95·0	82	179·6	129	264·2
—11	12·2	36	96·8	83	181·4	130	266·0
—10	14·0	37	98·6	84	183·2	131	267·8
— 9	15·8	38	100·4	85	185·0	132	269·6
— 8	17·6	39	102·2	86	186·8	133	271·4
— 7	19·4	40	104·0	87	188·6	134	273·2
— 6	21·2	41	105·8	88	190·4	135	275·0
— 5	23·0	42	107·6	89	192·2	136	276·8
— 4	24·8	43	109·4	90	194·0		

OF THE CENTIGRADE THERMOMETER
FAHRENHEIT'S SCALE.

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
137°	278·6°	183°	361·4°	229°	444·2°
138	280·4	184	363·2	230	446·0
139	282·2	185	365·0	231	447·8
140	284·0	186	366·8	232	449·6
141	285·8	187	368·6	233	451·4
142	287·6	188	370·4	234	453·2
143	289·4	189	372·2	235	455·0
144	291·2	190	374·0	236	456·8
145	293·0	191	375·8	237	458·6
146	294·8	192	377·6	238	460·4
147	296·6	193	379·4	239	462·2
148	298·4	194	381·2	240	464·0
149	300·2	195	383·0	241	465·8
150	302·0	196	384·8	242	467·6
151	303·8	197	386·6	243	469·4
152	305·6	198	388·4	244	471·2
153	307·4	199	390·2	245	473·0
154	309·2	200	392·0	246	474·8
155	311·0	201	393·8	247	476·6
156	312·8	202	395·6	248	478·4
157	314·6	203	397·4	249	480·2
158	316·4	204	399·2	250	482·0
159	318·2	205	401·0	251	483·8
160	320·0	206	402·8	252	485·6
161	321·8	207	404·6	253	487·4
162	323·6	208	406·4	254	489·2
163	325·4	209	408·2	255	491·0
164	327·2	210	410·0	256	492·8
165	329·0	211	411·8	257	494·6
166	330·8	212	413·6	258	496·4
167	332·6	213	415·4	259	498·2
168	334·4	214	417·2	260	500·0
169	336·2	215	419·0	261	501·8
170	338·0	216	420·8	262	503·6
171	339·8	217	422·6	263	505·4
172	341·6	218	424·4	264	507·2
173	343·4	219	426·2	265	509·0
174	345·2	220	428·0	266	510·8
175	347·0	221	429·8	267	512·6
176	348·8	222	431·6	268	514·4
177	350·6	223	433·4	269	516·2
178	352·4	224	435·2	270	518·0
179	354·2	225	437·0	271	519·8
180	356·0	226	438·8	272	521·6
181	357·8	227	440·6	273	523·4
182	359·6	228	442·4	274	525·2

WEIGHTS AND MEASURES.

GRAMMES.		GRAINS.	DECIGRAMMES.		GRAINS.
1	=	15·4346	1	=	1·5434
2	...	30·8692	2	...	3·0869
3	...	46·3038	3	...	4·6304
4	...	61·7384	4	...	6·1738
5	...	77·1730	5	...	7·7173
6	...	92·6076	6	...	9·2607
7	...	108·0422	7	...	10·8042
8	...	123·4768	8	...	12·3476
9	...	138·9114	9	...	13·8911

CENTIGRAMMES.		GRAINS.	MILLIGRAMMES.		GRAINS.
1	=	·1543	1	=	·0154
2	...	·3086	2	...	·0308
3	...	·4630	3	...	·0463
4	...	·6173	4	...	·0617
5	...	·7717	5	...	·0771
6	...	·9260	6	...	·0926
7	...	1·0804	7	...	·1080
8	...	1·2347	8	...	·1234
9	...	1·3891	9	...	·1389

METRES.		INCHES.	DECIMETRES.		INCHES.
1	=	39·37	1	=	3·937
2	...	78·74	2	...	7·874
3	...	118·11	3	...	11·811
4	...	157·48	4	...	15·748
5	...	196·85	5	...	19·685
6	...	236·22	6	...	23·622
7	...	275·59	7	...	27·559
8	...	314·96	8	...	31·496
9	...	354·33	9	...	35·433

CENTIMETRES.		INCHES.	MILLIMETRES.		INCHES.
1	=	·3937	1	=	·03937
2	...	·7874	2	...	·07874
3	...	1·1811	3	...	·11811
4	...	1·5748	4	...	·15748
5	...	1·9685	5	...	·19685
6	...	2·3622	6	...	·23622
7	...	2·7559	7	...	·27559
8	...	3·1496	8	...	·31496
9	...	3·5433	9	...	·35433

One kilogramme = 15434 grains.
One cubic centimetre = 0·0610 cubic inch.
One litre = 61·0271 cubic inches.

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,, 85, ,, 3 from bottom, *for* Ammonia, *read* Soda.
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THE END.

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